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Prevention Reference Manual: Overviews on Preventing and Controlling Accidental Releases of Selected Toxic Chemicals

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ABSTRACT

Concerns about the potentially disastrous consequences of accidental releases of toxic chemicals has led to increased interest in reducing the probability of effects of such releases. This manual, one of a series, presents an overview of the prevention of accidental releases of 13 specific chemicals, selected randomly from a larger EPA list. Potential hazards control in chemical processes is discussed, followed by a discussion of the chemicals and their key characteristics. These discussions are intended to be information capsules for quick reference. Formal methods of hazard identification and evaluation are discussed and their major features compared, and an overview of control principles for prevention, protection, and mitigation is presented.

While most of the principles of effective prevention, protection, and mitigation are generic, individual chemical properties, and the specific processes in which individual chemicals are produced or used, influence some of the details of how the principles are implemented. For example, while overpressure is a generic issue, it is a more important hazard for accidental releases for chemicals with high vapor pressures. Another example, is that, while the primary release hazard for one chemical may be due to its flammability, for another it may be due to its corrosiveness. Chemical specific process related issues pertinent to accidental releases of the individual chemicals are discussed.

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SECTION 1
INTRODUCTION

1.1 BACKGROUND

Increasing concern about the potentially disastrous consequences of accidental releases of toxic chemicals resulted from the Bhopal, India accident of December 3, 1984, which killed approximately 2,000 people and injured thousands more when a toxic cloud of methyl isocyanate was released. This tragedy led to worldwide concern about the potential for accidents of similar magnitude elsewhere. In the United States, the concern intensified when a major release of aldicarb oxime occurred soon thereafter from a chemical facility in Institute, West Virginia, fortunately without loss of life. These incidents clearly demonstrated the potential for disaster as the result of an accidental release of chemicals that have become a part of modern life; they also focussed attention on the fact that releases of chemicals from the facilities where they are manufactured, processed, used, or stored not only can occur, but do occur commonly.

The result was a new urgency in efforts to establish national programs to address chemical emergencies. The Chemical Emergency Preparedness Program (CEPP) of the U.S. Environmental Protection Agency (EPA), designed to foster planning and preparation within communities for serious releases of extremely hazardous substances from local chemical facilities, was launched nationally in November 1985. Concurrently, the Chemical Manufacturers Association (CMA) initiated the Community Awareness and Emergency Response Program (CAER) to encourage communication between industry and local communities about chemical hazards. By October 1986, the local planning encouraged on a voluntary basis by CEPP was made mandatory by Congressional enactment of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA). Title III of

SARA is entitled the "Emergency Planning and Community Right-to-Know Act of 1986."

The emergency planning provisions of Title III require communities to prepare for the possibility of accidents at facilities handling extremely hazardous substances. The "community right-to-know" provisions require industry to share information with communities about toxic chemicals present at a local facility. To enable communities to recognize the potential hazards associated with local chemical production or use, Congress included in Title III requirements for facilities to report regularly the presence of hazardous chemicals on site, as well as emissions of such chemicals to any environmental medium; air, water, or land (soil).

The overall thrust of all of these activities is to reduce the risk of harm to people, while at the same time ensuring that the people are aware of risks so that they may take actions of their own, if necessary, to reduce the risks.

1.2 PURPOSE OF THIS MANUAL

The purpose of this manual is to orient regulatory personnel and others involved in inspecting and otherwise evaluating potential toxic chemical release hazards to the fundamentals of release hazard control for some specific chemicals. It also guides the user to other technical literature for additional information. One specific purpose is to assist the EPA evaluation teams in a review of emergency systems mandated under SARA.

Section 305(b) of SARA requires that the EPA conduct a "review of emergency systems for monitoring, detecting, and preventing releases of extremely hazardous substances at representative domestic facilities that produce, use, or store extremely hazardous substances." The EPA must also prepare and present to Congress a report with recommendations for initiatives for the development of technologies and systems for monitoring, detecting, and preventing the accidental release of chemical substances, and for public alert systems that warn of an imminent release.

To prepare the report to Congress, the EPA is surveying a sample of domestic facilities which handle one or more of 20 chemicals selected from the SARA Section 302(a) list of "extremely hazardous substances." The 20 chemicals were selected from the list of extremely hazardous substances by the following procedure. First, EPA identified seven chemicals distinguished by their large production volumes, widely recognized hazards, involvement in past plant and transportation accidents, and generally recognized special handling procedures and controls. These chemicals -- ammonia, chlorine, hydrocyanic acid (hydrogen cyanide), hydrogen fluoride, methyl isocyanate, sulfur dioxide, and sulfur trioxide -- represent a wide range of toxicity, reactivity, flammability, and corrosivity hazards.

The remaining chemicals from the list of 20, discussed in this manual, were randomly selected by the U.S. EPA Office of Solid Waste and Emergency Response from subgroups of certain specified criteria (e.g., vapor pressure, ambient physical state, etc.) with the same proportion of chemicals in each physical state as the full list of extremely hazardous substances. Accordingly, two gases, seven liquids, and four solids were chosen. The seven liquids were selected to represent a range of vapor pressures (less than 1 mm Hg to greater than 100 mm Hg) at 25°C. These chemicals are: acrylonitrile, benzenearsonic acid, benzotrichloride, chloroacetic acid, furan, hydrazine, hydrogen sulfide, methiocarb, mechlorethamine, methyl bromide, sodium azide, tetraethyl tin, and trichoroacetyl chloride.

The EPA evaluated each chemical selected in this manner with respect to factors influencing the type of monitoring, detection, prevention, and mitigation measures likely to be employed in handling the chemical: corrosivity, flammability, and reactivity ratings; manufacturing, processing, and use volumes; number of sites where the substance may be manufactured, processed, or used; physical state and volatility; and information on past accidental releases. In considering these factors, the EPA tried to ensure that a wide range of industrial activities would be covered in the review and that the review addressed only chemicals produced or handled in sufficient volume to warrant inclusion. Based on this final screening, one of the chemicals initially selected, 3-chloropropionitrile, was dropped and hydrazine, which meets the same physical property criteria (liquid, medium vapor pressure), was selected as a replacement.

A written questionnaire has been sent to a sample of domestic facilities which produce, use or store one or more of the 20 extremely hazardous substances. The questionnaire has two purposes: 1) to gather additional data on available technologies and procedures and practices for monitoring, detection, prevention, and mitigation of accidental releases; and 2) to determine which technologies, operating procedures, and management practices are being used, and why. Trained inspectors will visit a limited number of the surveyed facilities to obtain in-depth information, as well as to corroborate the survey responses.

It is intended that this manual provide information useful to EPA inspection or evaluation teams for release hazards of some of the specific chemicals at facilities they will be visiting and for reviewing survey questionnaires from an even greater number of facilities. In addition to descriptive text, tables on chemical and process specific hazards are provided to provide easy reference for the user. It is intended that this manual be used in conjunction with other manuals in a set of prevention reference manuals whose overall purpose is to summarize the major concepts of release hazard identification and control so that the probability and consequences (risk is the product of probability and consequences; risk = probability x consequences) of accidental toxic chemical releases can be reduced. The volumes in the series include: a User's Guide, or overview for controlling accidental releases of air toxics; a Control Technologies manual describing the methods available for preventing and protecting against accidental toxic chemical releases; and a series of chemical-specific manuals describing the release hazards associated with certain toxic chemicals (chlorine, hydrogen fluoride, hydrogen cyanide, sulfur dioxide, ammonia, sulfur trichloride, methyl isocyanate). A series of chemical-specific manuals for the South Coast Air Quality Management District of California has also been prepared (chlorine, hydrogen fluoride, hydrogen cyanide, sulfur dioxide, ammonia, carbon tetrachloride, and chloropicrin). A manual on mitigation technologies for controlling accidental releases of air toxics is being prepared.

The PRM-Chemical Specific manual actually consists of a number of individual volumes for specific chemicals, while this manual provides an overview of hazard control for thirteen toxic chemicals: acrylonitrile, benzenearsonic acid, benzotrichloride, chloroacetic acid, furan, hydrazine, hydrogen sulfide, mechlorethamine, methiocarb, methyl bromide, sodium azide, tetraethyl tin, and trichloroacetyl chloride.

The PRM-User's Guide is a general introduction to the subject of toxic chemical releases, overview of the accidental release problem, and summary of methods commonly used in hazard identification, and evaluation and principles of hazard control. The PRM-Control Technologies volumes address prevention, protection and mitigation measures which can generally be applied to reduce the probability and consequences of an accidental toxic chemical release. Taken together, the PRM series stresses the importance of technology, management and operations in achieving this goal. Used by qualified technical personnel, these manuals, in conjunction with other knowledge and experience, should provide the hazard orientation required to effectively evaluate equipment, systems, and procedures in facilities manufacturing, using, or storing toxic chemicals.

Since the purpose of the PRM series is to summarize the major concepts of release hazard control, the reader is referred to other information sources for more detailed discussions. Other sources include manufacturers and distributors of the various chemicals and technical literature on loss prevention in facilities handling toxic chemicals. Examples of technical literature include the American Institute of Chemical Engineering (AIChE) Loss Prevention Series and AIChE's Center for Chemical Process Safety publications.

The remainder of this manual contains two sections. Section 2 discusses release hazard control which begins with hazard identification and is the application of specific measures for pre-release prevention and protection, and post-release mitigation. In general, many of the technological, operational, and managerial aspects of hazard control are applicable to toxic chemicals in general. Section 3 presents an overview of chemical specific hazards that can contribute to a release. Topics discussed are: physical, chemical, and toxicological properties; information on the manufacture and use, including facility descriptions where appropriate; hazards associated with the various processes; and hazard prevention and control information specific to the chemical. Appendix A is a glossary of key technical terms that might not be familiar to all users of the manual. Appendix B presents selected conversion factors between metric (SI) and English measurement units.

SECTION 2
HAZARD CONTROL

Hazard identification is the first step in hazard control. Section 2.1 provides an overview of hazard identification and discusses two of the most commonly applied hazard identification methodologies. Once hazards are identified, specific measures may then be taken to control them.

General pre-release prevention, protection and mitigation measures are addressed in Section 2.2. Administrative and operational, as well as technological measures are covered in Section 2.2, since the prevention of toxic chemical accidental releases and a reduction in the severity of adverse effects on people after a release involves facility management and operational practices in addition to technology. Section 2.3 concludes the discussion of the mitigation aspect of hazard control by examining the use of models in simulating the movement of hazardous vapor or gas clouds. Models can be used as planning tools for predicting the effects of various accidental release scenarios and as emergency response tools aiding decision-making during an actual release event.

2.1 HAZARD IDENTIFICATION

The first step in hazard control on a specific process or facility is hazard identification. A publication of the American Institute of Chemical Engineers (AIChE) on guidelines for hazard evaluation lists the following methods of formal hazard identification (1):

- Checklists,
- Safety Review,
- Relative Ranking,
- Preliminary Hazard Analysis,

- What-If Analysis,
- Hazard and Operability Studies,
- Failure Modes, Effects, and Criticality Analysis,
- Fault Tree Analysis,
- Event Tree Analysis,
- Cause Consequence Analysis, and
- Human Error Analysis.

For an overview summary of the key features and use of these methods, see other manuals in this series. The reader may also refer to an AIChE publication for more detailed descriptions of the methodologies (1). In addition, these methods are discussed in other technical literature (e.g. Reference 2) and the AIChE and other organizations present short courses on hazard identification at national meetings and special symposia and conferences.

In a survey by the Chemical Manufacturer's Association, "What-If" analyses and Hazard and Operability (HAZOP) studies were named as the methods most often used for hazard identification (3). Key features of these two methods are summarized below.

2.1.1 "What If" Analysis

A "What If" analysis systematically considers the consequences of unexpected abnormal events that may occur in a process facility. It can include design, construction, operating, or other deviations from the norm. A "What If" examination can include all parts of a process facility. Its comprehensiveness and success depends on the experience of the staff conducting the analysis. Table 2-1 lists the purpose, time of use, type of results, staff requirements and relative cost of the "What If" analysis as well as the HAZOP method discussed next.

TABLE 2-1. SUMMARY OF KEY FEATURES OF "WHAT IF" AND HAZOP ANALYSES

METHOD	What If Analysis	HAZOP
PURPOSE	Identify hazards Identify event sequences Identify possible methods of risk reduction	Identify hazards Identify operability problems Identify event sequences Identify possible methods of risk reduction
WHEN TO USE	Process development Pre-startup Operation	Late design Operation
NATURE OF RESULTS	Qualitative	Qualitative
STAFF SIZE	Small - Moderate	Moderate - Large
RELATIVE COST	Moderate	Moderate - High

2.1.2 Hazard and Operability (HAZOP) Study

A HAZOP study can identify process hazards and operability problems. A multidisciplinary team conducts a HAZOP study by searching for deviations from intended design and operating conditions. The team carefully examines each individual stream and component of a process facility using standard design "guide words" applied to each process variable such as flow, for example. Consequences of deviations expressed by the guide words are identified. In this way, hazards, some of which may result in accidental releases, are identified. Key features of the methodology are shown in Table 2-1. Example guide words are presented in Table 2-2.

2.2 PRE-RELEASE PREVENTION, PROTECTION, AND POST-RELEASE MITIGATION

2.2.1 General Considerations

Prevention of accidental releases and their adverse consequences relies on a combination of administrative, operational, and technological measures that apply to the design, construction, operation and maintenance of facilities that manufacture, use and store toxic chemicals. These measures are based on various principles and considerations that can be grouped as follows:

- Pre-release Prevention
  - Process design
  - Physical facility design
  - Operating and maintenance practices (including management);

- Pre-release Protection systems; and

- Post-release Mitigation systems.

In each of these areas, defined subsequently, specific factors are considered that could lead to a process upset (e.g., overpressure) or

TABLE 2-2. EXAMPLE GUIDE WORDS AND CORRESPONDING DEVIATIONS FOR HAZOP ANALYSIS

Guide Word	Deviations
None	No forward flow, material present, or action when there should be.
More of	More of any relevant physical property than there should be, e.g., higher flow (rate or total quantity), higher temperature, higher pressure, higher viscosity, etc.
Less of	Less of any relevant physical property than there should be, e.g., lower flow (rate or total quantity), lower temperature, lower pressure, etc.
Part of	Composition of system different from what it should be, e.g., change in ratio of components, component missing, etc.
More than	More components present in the system than there should be, e.g., extra phase present (vapor, solid), impurities (air, water, acids, corrosion products), etc.
Other than	What else can happen apart from normal operation, e.g., startup, shutdown, uprating, low running, alternative operation mode, failure of plant services, maintenance, catalyst change, etc.
Reverse	Variable or activity is reverse of what it should be, e.g., reverse flow.

operational failure (e.g., opening a drain valve) that could directly cause a release of the chemical to the environment, or result in an equipment failure (e.g., pipe rupture) that would then cause the release. At a minimum, equipment and procedures should be designed, constructed, operated, and maintained in accordance with applicable codes, standards, and regulations. In addition, stricter equipment and procedural specifications may be necessary to reduce the probability or consequences of accidental releases below levels that still might exist in spite of such codes, standards, or specifications.

The following subsections define and discuss prevention, protection, and mitigation in a little more detail. Further discussion can be found in other volumes of this series and in the technical literature.

2.2.2 Pre-Release Prevention

Pre-release prevention refers to measures taken to reduce the probability than an accidental release of a toxic chemical will occur. Prevention begins with process design and is an inherent part of each phase of activity in the life cycle of a process facility, from the initial design through facility startup, routine operation, and shut down. The most fundamental principles of release prevention include process design, physical facility design, and operations (which here is defined to include management and maintenance practices).

Process Design--

Process design considerations involve several fundamental principles applied to the process materials, process variables, and equipment. These principles are addition, substitution, deletion, and redundancy (or duplication). Each process, chemical, operation, or piece of equipment in a process facility should be viewed in terms of how changes based on these qualities may lead to a reduction in the probability of an accidental release. For example, substitution might involve the replacement of a toxic chemical with one less toxic. Duplication or redundancy might involve the use of a second thermocouple to measure a critical temperature. In each case, a hazard reduction is achieved. The substitution reduces the probability of the toxic release to zero by removing the chemical from the process. In the thermocouple example, the second thermocouple serves as a backup to the first, which improves the chances for controlling a process upset. This reduces the chance that an upset can lead to an accidental release.

There are a number of fundamental aspects of process design and operation which are an inherent part of process control and essential to reducing the probability of process upsets and accidental releases. Each of these are discussed below.

Control Characteristics of the Process--Good process control, including the interaction of human operators with the process system, is basic to successful process operations. Process control is achieved by manipulating the process variables of flow, temperature, pressure, composition, and quantity. Loss of containment through loss of control occurs when a process variable exceeds the physical limits of the containment system. Process control systems, both strategies and hardware, may differ in their control characteristics and ability to reduce the probability of an accidental release. A process control system performs the following functions: measurement, normal control, and emergency or protective control. How each of these is achieved determines the control effectiveness of the control system in release prevention.

Process Characteristics and Chemistry--Fundamental process changes can often reduce the inherent process hazards by reducing in-process inventories of toxic materials and by reducing the severity of operating conditions, such as temperature and pressure.

Pressure Control--Pressure above or below the design intent of a process can increase the probability of an accidental chemical release. Overpressure can cause the opening of a relief device and the discharge of a toxic chemical to the environment. Either can cause physical failure of process or storage equipment and loss of containment. Generally, overpressure is considered more hazardous than underpressure, but both should be considered as potential causes of a hazardous release.

Three related process events--thermal expansion, excess material generation and flow blockage-can lead to loss of pressure control. One example of this first hazard is posed by liquid-full equipment; equipment with little or no vapor space above the liquid. Liquid expansion with heating can cause equipment rupture. An example of excess material generation is the continued heating of a vaporizing liquid in a closed vessel, increasing the pressure in the vessel. An example of excess pressure can be created by flow blockage when a positive displacement pump is used to pump a liquid.

Flow Measurement and Control--Process hazards associated with flow involve deviations that cause the flow to be too low, too high, reversed or fluctuating. Flow deviations can result in process hazards and accidental releases due to: overheating, inadequate heating, incorrect feed rates to reacting systems, overfilling of vessels, unwanted siphoning of liquids, unintended chemical or physical reactions, obstruction of vent lines, contamination by leakage, excessive back pressure on relief valves, severe pulsations leading to construction materials' fatigue, and a reduction in process controllability.

Temperature Control--Loss of temperature control may result in an exothermic runaway reaction which can lead to an accidental release through direct equipment failure from overheating or overpressure. Since the volume of gases, and to some extent liquids, depends on temperature, a loss of temperature control will often result in a loss of pressure control.

Quantity Control--The two primary objectives of quantity control are to achieve proper process material ratios and the proper level and/or weight of materials in process or storage vessels. Failure to achieve these objectives could result in overfilling or overpressuring of equipment.

Mixing--A loss of agitation is usually the primary hazard in mixing systems. Loss of agitation and mixing can cause: incomplete reactions or formation of unwanted by-products; reactant accumulation in poorly mixed zones; and poor heat transfer. These conditions can initiate or be a part of a chain of events leading to an accidental release.

Composition Control--When a stream's composition varies from design specifications, its chemical and physical properties also vary. The consequences are process specific but may be contributory to a loss of process control by affecting the other process variables already discussed. A common and significant manifestation of poor composition control is unexpected corrosion.

Physical Facility Design--

Physical facility design covers process and storage equipment, siting and layout, and transfer/transport facilities. Vessels, piping and valves, process machinery, instrumentation, and factors such as the location of process systems and individual equipment items are all considered. The following subsections review various aspects of physical facility design, beginning with a discussion of materials of construction. This section on physical plant design is not intended to provide detailed specifications for the design of facilities handling the toxic chemicals discussed in this manual; it is intended to illustrate major considerations of release prevention. Additional discussion can be found in other volumes in this series.

Equipment--The primary function of storage and process equipment is containment. Direct equipment failure and loss of containment can occur due to rupture, leaks at joints and connections such as separated flanges, actuated relief valves or rupture disks. Equipment failure such as failed pumps or control valves, while not a direct loss of containment, can cause process upsets and initiate a chain of events leading to an accidental release. Special hazards associated with equipment are noted below.

Materials of Construction--The materials of construction required for process equipment depend on the compatibility of the chemicals with various materials under the operating conditions of each specific process. This compatibility can vary with temperature, pressure, and composition. As is discussed for the individual chemicals in Section 3, materials compatible with the chemical at ambient conditions were noted. These conditions would represent a starting point, or minimum basis, for materials selection. Selecting the wrong material of construction can lead to equipment failure from corrosion, erosion, or mechanical wear. Process fluid characteristics such as alkalinity, acidity, solvency, abrasiveness, and reactivity must be considered with both normal pressure and temperature as well as extremes, and with the frequency and magnitude of temperature and pressure fluctuations in selecting materials of construction.

Even if an appropriate material is specified in the original design, a contractor or vendor may substitute one material for another, or maintenance personnel may replace a part with one made of an inappropriate material. Incorrect substitutions are potentially dangerous and can cause a system failure leading to a release. Ensuring that the correct materials are selected and used begins with the initial design specifications but requires proper supervision from design through maintenance during the life of an operating facility.

The most common materials of construction are carbon steel and various stainless steels. Other metals and alloys are sometimes required for certain corrosion and operating conditions. Plastics and glass as liners of process equipment also are used where corrosion is a problem. Some process equipment is also fabricated from plastics and glass. Such equipment may be more easily broken than metal equipment, and this must be taken into consideration when toxic chemicals are involved. Liner materials have been noted in the individual chemical summaries of Section 3 where applicable. No general principles were found in the technical literature concerning the use of plastics with toxic chemicals.

Vessels--Vessels, which include both process and storage equipment, include all major items of equipment containing significant inventories of a toxic chemical. As used here, vessels include tanks, reactors, heat exchanger shells, columns, and similar equipment. Vessels may be atmospheric, pressurized, or operate under vacuum.

Vessels must be protected from overpressure, overfilling, overheating, and corrosion. Prevention of accidental releases depends on proper initial design of the vessel and process system of which it is a part, as well as on proper operation and maintenance while it is in service.

Overpressure protection of vessels is commonly provided by relief devices. These include rupture disks and relief valves. Such devices protect against catastrophic rupture or explosion by allowing a controlled release of overpressurized vessel contents. The type of device used depends on the vessel service and potential causes of the overpressure. Relief devices for overpressure caused by fire or other overheating may be fusible plugs that melt at a predetermined temperature. While these devices are designed to prevent a catastrophic sudden release of vessel contents, a significant release can still occur unless the relief device discharge is routed to a protection system such as an emergency vent scrubber or flare for gases, vapors, or particulate fumes, or overflow catch tanks for liquids

Overfilling can be prevented by using level-sensing devices and alarms, including these devices with automatic feed shut-off interlocks, pressure relief devices, and well-trained operating personnel. The overfill relief would discharge to an overflow catch tank or to another suitable receiver.

Careful attention should be given to vessel corrosion; suitable materials of construction, adequate corrosion allowances should be provided. Special attention should be given to welds and the possibility of external corrosion under insulation.

Piping--As used here, the term "piping" describes three closely associated equipment components: piping, fittings, and valves. Straight piping can be drawn, rolled and welded, or cast. Fittings, used to connect various pipe sections or to connect pipe to another piece of equipment, to change the direction of flow, or to provide a branch, are forged or cast. The method of fabrication and the material of which the pipes and fittings are made determine the ultimate strength or pressure rating in different types of service. Each type of pipe has definite limitations on temperature, pressure, and chemical environment. Specific information can be obtained from vendors and in standard technical references (e.g. Reference 4).

Valves, used to regulate the flowrate or direction of flow through lines, can be ball valves, gate valves, globe valves, plug valves diaphragm valves, butterfly valves, and check valves. Fabrication and materials of construction considerations are similar to those just discussed for pipe and fittings.

In addition to the considerations of pressure, temperature, and chemical environment for piping selection and design for toxic chemical service, simplicity of design is desirable. The number of joints and connections should be minimized. Piping should be securely supported to avoid excess vibration and overstress due to mechanical loading and thermal gradients. Piping should be constructed to allow room for thermal expansion and should be protected from exposure to fire and temperatures that exceed design limits. Long pipe runs should be sloped, with drainage provided at the low points.

Special attention must be paid to piping joints, whether threaded, flanged or welded. For toxic chemicals, special precautions must be taken to ensure that threaded joints are fully threaded and properly installed, that the correct gaskets and flanges are used for flanged joints, the joints are properly torqued, and that welded joints are inspected for weld integrity.

Valves in piping systems should be placed so that leaking or ruptured pipes and equipment up or downstream of the values may be isolated, but no section of piping should be isolated from some form of overpressure relief or expansion chamber while in service. Valves should be easy to remove and maintain, and should have high-quality leak-tight packings or be leakproof, like a diaphragm, or bellow-sealed.

Process Machinery--Process machinery refers to rotating or reciprocating equipment used in the transfer or processing of a chemical. This includes pumps, blowers, and compressors that may be used to move a liquid or gas, and items such as screw and belt conveyors for solids.

Pumps--Many of the general considerations for piping and valves also apply to pumps. Pump failures can be initiating or propagating events in a chain of events leading to accidental releases. To ensure that a given pump is suitable for a given service application, the system designer should obtain information from the pump manufacturer certifying that the pump will perform properly in the intended application. Materials of construction is always an important consideration for pumps since they contain moving parts.

Pumps should be installed dry and oil-free to prevent process contamination with oil. Net positive suction head (NPSH) considerations are especially important for pumping a liquid near its boiling point. In critical applications where a pump failure could lead to an accidental release, the pump supply vessel should have high and low level alarms; the pump might even be interlocked to shut off at low supply level or low discharge pressure.

The type of pump selected depends on pumping requirements and process operating conditions. Centrifugal, rotary, and positive displacement pumps are typically used. In some situations, the potential for seal leakage of a toxic or flammable material precludes standard rotating shaft seals. Some seals use a flushing fluid to prevent entry of the process fluid into the seal area. Pumps using stuffing boxes and packing are often provided with double-packed seal chambers designed to prevent the toxic material from contacting any reactive material. These chambers can be purged with an appropriate inert fluid such as dry and oil-free nitrogen, or a suitable seal liquid. The seal gas pressure should exceed the tank pressure by an appropriate margin. Canned-motor pumps, vertical submersible pumps, magnetically coupled pumps and diaphragm pumps eliminate shaft seals altogether.

Canned motor pumps have the motor housing integral with the pump casing. Here, the process liquid actually serves as the bearing lubricant. An alternative is the vertical pump often used on storage tanks. The advantage of these pumps, which consist of a submerged impeller housing connected by a drive shaft to the motor, is that the shaft seal is above the maximum liquid level (and is therefore not wetted by the pumped liquid) and the pump is self priming because the liquid level is above the impeller.

Magnetically-coupled pumps replace the drive shaft with a rotating magnetic field as the pump-motor coupling device. Diaphragm pumps are positive displacement units in which a reciprocating flexible diaphragm drives the fluid. This arrangement eliminates exposure of packing and seals to the pumped liquid. However, a major consideration in the application of such pumps is that at some point, diaphragm failure will probably occur.

Improper operation of pumps, i.e. cavitation, running dry, and deadheading, can cause pump damage and failure. Cavitation can be a problem in pumping materials with low boiling point because of their tendency to vaporize easily. If cavitation is allowed to occur, pitting and eventual serious damage to the impeller can result. Running a pump dry because of loss of head in a feed tank, for example, can seriously damage a pump. Finally, pumping against a closed valve, deadheading, can have serious ramifications. A pump bypass and recycle loop back to the feed container avoid such an occurrence.

Deadheading is a special concern with positive displacement pumps. To prevent rupture, positive displacement pumps commonly have a pressure relief valve that bypasses to the pump suction. Centrifugal pumps often have a recycle loop back to the feed container.

Compressors--Reciprocating, centrifugal, liquid-ring rotary, and non-lubricated screw compressors are used to transfer gases. Like pumps, compressors have the potential for shaft seal leakage. Overheating can cause real damage and leakage. Heat sources in a compressor include the heat of compression as well as the heat generated through mechanical friction. Most multistaged compressors can be equipped with intercoolers that limit heat buildup and increase compressor efficiency by reducing the volume of gas going to the next compression stage.

While it is sometimes possible to avoid using rotary shaft seals with pumps, rotary compressors usually require seals. Special seals such as double labyrinth seals are often used. These seals have a series of interlocking touch points which, by creating many incremental pressure drops, reduce total leakage. Also, to further reduce leakage, dry air is injected into the seal. In the event of deadheading, a compressor discharge can have a pressure relief mechanism that vents to the compressor inlet or to a scrubber system. The former appears to be satisfactory for a short term downstream flow interruption. Where a sustained interruption might occur, relief to a scrubber system may be safer. Positive displacement compressors and pumps must always be equipped with non-isolatable overpressure relief as close to the discharge as possible.

Solids' Conveyors--Conveyors for solids may not be as critical to accidental releases as are pumps and compressors because conveyors do not pressurize a fluid. They are included in this discussion only because where a toxic solid chemical is processed, used, or stored, conveyors may be a type of process machinery required for the transfer of the solids. The primary prevention consideration for conveyors is that they be limited in their size as much as possible to avoid large in-process inventories of dry toxic materials. They should also be enclosed and have high-quality dust control equipment associated with their vents.

Plant Siting and Layout--The siting and layout of a facility using a toxic chemical requires careful consideration of numerous factors, including other processes in the area, the proximity of population centers, prevailing winds, local terrain, and natural external events such as flooding.

The siting of facilities and individual equipment items within facilities should minimize personnel exposure, both plant and public, in the event of a release. Since other siting considerations are also important, there may be trade-offs between this requirement and others in a process, some directly related to safety. Siting should provide ready ingress or egress in the event of an emergency and also take advantage of barriers, either man-made or natural, that could reduce the consequences of releases.

Layout refers to the placement and arrangement of equipment in the process facility. Some general layout considerations pertinent to accidental release prevention include:

- Inventories of a toxic chemical should be kept away from sources of fire or explosion hazard;

- Vehicular traffic near toxic chemical process or storage areas should be minimized;

- Where such traffic is necessary, precautions should be taken to reduce the chances for vehicular collisions with equipment, especially pipe racks carrying the toxic chemical across or next to roadways;

- Piping containing a toxic chemical preferably should not be located adjacent to other piping that is under high pressure or temperature;

- Toxic chemical storage facilities should be segregated from the main process unless the hazards of pipe transport are determined to outweigh the hazard of the storage for site-specific cases;

- Toxic chemical storage facilities should be situated away from control rooms, offices, utilities, storage, and laboratory areas;

- In the event of an emergency, there should be at least two means of access to the facility for emergency vehicles and crew.

Various techniques available for formally assessing plant layout should be considered when planning high-hazard facilities handling a toxic chemical (2). These techniques allow a systematic evaluation of key siting and layout factors.

2.2.3 Protection

Pre-release protective systems include measures taken to capture or destroy a toxic chemical before there is an uncontrolled release to the environment after a release from primary containment has occurred. This subsection describes three types of protection technologies for secondary containment, capture, neutralization, or destruction:

- Enclosures;
- Flares; and
- Scrubbers.

Table 2-3 lists air toxic protection technologies applicable to the various toxic chemicals discussed in this manual. A brief discussion of these

TABLE 2-3. SOME AIR TOXIC RELEASE PROTECTION TECHNOLOGIES APPLICABLE TO TOXIC CHEMICALS DISCUSSED IN THIS MANUAL

Chemical (physical state)[a]	Protection Technology[b]				
	Enclosure	Flare	Venturi Scrubber	Packed Bed Scrubber	Spray Tower Scrubber
Acrylonitrile (L)	X	X	X	X	X
Benzenearsonic Acid (S)	X		X		X
Benzotrichloride (L)	X		X	X	X
Chloroacetic Acid (S)	X		X		X
Furan (L)	X	X	X	X	X
Hydrazine (L)	X	X	X	X	X
Hydrogen Sulfide (G)	X	X	X	X	X
Mechlorethamine (L)	X				
Methiocarb (S)	X		X		X
Methyl Bromide (G)	X	X	X	X	X
Sodium Azide (S)	X		X		X
Tetraethyl Tin (L)	X		X		X
Trichloroacetyl Chloride (L)	X		X	X	X

Notes:

[a] Physical state of 70°F. S = Solid. L = Liquid. G = gas.

[b] The applicability of a protection technology depends on the physical state. It should be borne in mind that solids and liquids at ambient conditions can still cause a vapor air toxic hazard at elevated temperatures as may be found in some processes. Some air toxic vapors will also be caused by liquids at ambient conditions. Also, some solids may form fine dusts or fumes which could be captured by scrubbers prior to an accidental release

protection technologies follows. More detailed information on these systems can be found in other volumes in this series.

Enclosures--

Enclosures refer to containment structures that capture any toxic material spilled or vented from storage or process equipment, thereby preventing immediate discharge of the chemical to the environment. The enclosures contain a spilled liquid or solid until it can be transferred to other containment, discharged at a controlled rate that would not be injurious to people or to the environment, or transferred at a controlled rate to a scrubber for neutralization or a flare for destruction.

Specially designed enclosures for either storage or process equipment do not appear to be widely used for temporary containment of toxic materials. The desirability of an enclosure depends partly on the frequency with which personnel must be involved with the equipment. A common design rationale for not having an enclosure where toxic materials are used is to prevent the accumulation of toxic concentrations of a chemical within a work area. Where flammable materials are involved, an additional concern is the accumulation of flammable gases or vapors in the range of explosive limits. However, if the issue is protecting the community from accidental releases, then total enclosure may be appropriate. Enclosures should be equipped with continuous monitoring equipment and alarms. Alarms should sound whenever lethal or flammable concentrations are detected. Enclosures for flammable materials should be equipped with adequate fire protection.

Care must be taken when an enclosure is built around pressurized equipment. It would not be practical to design an enclosure to withstand the pressures associated with the sudden failure of a pressurized vessel. An enclosure would probably fail because of the pressure created from such a release and could create an additional hazard. If an enclosure is built around pressurized equipment, it should be equipped with some type of explosion protection, such as rupture plates designed to fail before the entire structure fails.

Suitable containment structures might be concrete or corrugated metal buildings. An enclosure would have a ventilation system designed to draw in air when the building is vented to a scrubber or flare. The bottom section of a building used for stationary storage containers should be liquid-tight to retain any toxic material that might be spilled. Buildings around rail car unloading stations do not lend themselves to effective liquid containment; however, the floor of the building could be excavated several feet below the track level while the tracks are supported at grade in the center, creating a contained space.

While the use of enclosures for secondary containment of spills or releases of toxic material are not widely used, they can be considered as a possible protection technology for areas near especially sensitive receptors.

Flares--

Flares are used in the chemical process industries to dispose of intermittent emissions of some toxic waste gases from process upsets. The flare burns the waste gases, forming less toxic product gases. Flares are distinguished from other process combustion devices, such as incinerators, by their design to handle extreme flow rate variations and their unenclosed combustion zone.

The two common styles are elevated and enclosed ground flares. The height of an elevated flare (often several hundred feed) is determined by safety considerations for the surrounding areas because of the high temperatures and heat radiation at maximum gas rates. Enclosed ground flares consist of stages of multiple burner assemblies surrounded by refractory walls and acoustical insulation. They are generally used for small to medium flow rate applications. The elevated flare is used for larger gas flows. Often, an enclosed ground flare will be used in conjunction with an elevated flare for optimum operation.

Several design characteristics of flare systems are important when considering their use as protection against accidental chemical releases. The design of flares is dictated by the desire to:

- Operate the flare safely over a wide range of gas flowrates; and

- Have acceptable emissions of radiant heat, toxic and flammable materials, and noise.

A fundamental flare design variable is exit velocity. At maximum flow, the flame should not leave the burner tip or be blown out. This is achieved by limiting the exit velocity. EPA has published a set of flare requirements calling for 98 percent destruction efficiency of flared chemicals using a steam assisted flare (5). The addition of an accidental release discharge to an existing flare must not cause the maximum flow to be exceeded, which is especially of concern when venting toxic materials since exceeding the maximum design flow could lead to flame-out and an uncontrolled toxic discharge.

Flares can be useful protection against accidental releases of some toxic materials. However, because of potentially dangerous secondary hazards, their use requires a thorough analysis of each application.

A flare system can be used to protect against accidental releases in two ways. The first is to use an existing flare system. The second is to use a dedicated "emergency" system. In essence, a flare system is a pipe transporting flammable gases to a flame at the exit. As long as the flame remains at the end of the pipe, the system operates safely. The flame can enter the pipe if air or oxygen is present in the fuel above a certain concentration. In a dedicated flare system, the entire collection network would have to be continually purged to prevent the risk of an explosion when an accidental release occurred.

Since the flare collection system operates under a positive pressure (above atmospheric), release rates through an emergency relief valve discharging to a flare may be less than direct discharge to the atmosphere because of the increased back pressure. In some instances, it is conceivable that the slight delay in reducing the pressure in a vessel may cause tank damage, which may be especially important when rupture disks blow. A sudden overpressurization of the flare collection system because of a massive accidental release could damage the pipes or potentially affect the venting of other process units. Table 2-4 summarizes the factors that should be considered to prevent accidental chemical releases when using a flare system.

The rationale for using flares to protect against accidental chemical releases is that flaring reduces the effects of an atmospheric emission from a process vessel. As long as the integrity of the flare system is not compromised, some lessening of the overall environmental impact would be expected. It is difficult to estimate the destruction and removal efficiency (DRE) of flares because of the many variables associated with their operation. Numerous studies have been conducted to determine the operational performance of flares. Although EPA has published a set of flare requirements to ensure 98 percent or greater destruction of the gases (5), in an emergency condition these conditions might not be met.

Because of the variable flow capacity, high temperature, high gas velocity, and usual remote location, using a flare as a protection measure for accidental chemical releases of some toxic materials can be highly effective. Small or isolated vessels that use a process that does not require normal venting of a flammable gas, and that employ relief valves and rupture disks that may have never been used, can be connected to a flare system to prevent accidental releases.

TABLE 2-4. IMPORTANT CONSIDERATIONS FOR USING FLARES TO PREVENT ACCIDENTAL CHEMICAL RELEASES

- Maximum flow rate - will it cause a flame blowout?
- Possibility of air, oxygen, or other oxidant entering system?
- Is gas combustible - will it smother the flare?
- Will reactions occur in the collection system?
- Can liquids enter the collection system?
- Will liquids flash and freeze, overload knockout drum or cause rain fire?
- Is back pressure of collection system dangerous to releasing vessel?
- Is releasing vessel gas pressure or temperature dangerous to collection system?
- Will acids or salts enter the collection system?
- Will release go to an enclosed ground or elevated flare?
- If toxic is not destroyed, what are the impacts on the surrounding community?

Scrubbers--

Scrubbers are a traditional method for absorbing toxic materials from process streams. They can be used to control the release of the toxic materials from vents and pressure relief discharges from storage equipment, process equipment, or secondary containment enclosures, and they can be used for many gases, vapors, or particulate matter.

A toxic material discharge can be contacted with an aqueous scrubbing medium in any of several types of scrubbing devices. Depending on the toxic material, an alkaline or acidic solution may be required for effective absorption because absorption rates with water alone would require high liquid-to-gas ratios. However, water scrubbing can be used in a make-shift scrubber in an emergency.

Examples of scrubber types that might be appropriate include spray towers, packed bed scrubbers, and venturis. Other types of special designs might be suitable. Whichever type of scrubber is selected, a key consideration for emergency systems is the design flow rate. A conservative design would use the maximum rate expected from an emergency.

Whatever type of scrubber is selected, a complete system includes the scrubber itself, a liquid feed system, and reagent makeup equipment. If such a system is used to protect against emergency releases, how it would be activated in time to respond to an emergency load must be considered. The approach of some process facilities is to maintain a continuous circulation of scrubbing liquor through the system, which may be practical where the emergency scrubber also serves as a routine vent scrubber. For many facilities, this would not be practical and the scrubber system might be tied into a trip system that would turn it on when needed.

Venturi scrubbers have an advantage when the scrubbing system must be activated by a trip system. A venturi scrubber can create its own draw of vapor by the flow of the liquid. Thus a trip system need only turn on the flow of liquid to the scrubber, rather than turn on the flow of liquid and start up a blower, as would be required by other types of scrubbing systems.

Another approach is the drowning tank, where the toxic material vent is routed to the bottom of a large tank of uncirculating scrubbing medium. The drowning tank does not have the high contact efficiency of the other scrubber types; however, it provides substantial capacity on demand as long as the back pressure of the hydrostatic head does not create a secondary hazard--by impeding an overpressure relief discharge, for example.

2.2.3 Post-Release Mitigation

Post-release mitigation includes measures taken to reduce the severity of the adverse effects of a hazardous chemical release. If, in spite of all precautions, a toxic chemical release occurs, the first priorities are to rescue workers in the immediate vicinity of the accident, to evacuate persons from downwind areas, to determine the source of the release, and to stop the release if possible. The next concern is to divert, limit, or disperse the spilled or released chemical to reduce the atmospheric concentration and the area affected by the chemical. The mitigation technology chosen for a particular chemical depends on the specific properties of the chemical i.e., its flammability, toxicity, reactivity, and those properties that determine its dispersion characteristics in the atmosphere.

A post-release mitigation effort requires that the source of the release be accessible to trained plant personnel; therefore, the availability of adequate personnel protection is essential. Personnel protection will typically include such items as portable breathing air and chemically resistant protective clothing.

Mitigation technologies include such measures as physical barriers, basins, water sprays and fogs, and foams. Table 2-5 lists typical mitigation

TABLE 2-5. TYPICAL MITIGATION TECHNOLOGIES APPLICABLE TO TOXIC CHEMICAL RELEASES

Chemical (physical state)[a]	Mitigation Technology[b] Containment Dikes	Basin	Flotation Devices and Foams	Water Sprays and/or Steam Curtains	Alkaline Sprays
Acrylonitrile (L)	X	X	X	X	
Benzenearsonic Acid (S)	X				
Chloroacetic Acid (S)	X	X	X	X	X
Hydrazine (L)	X	X	X	X	
Mechlorethamine (L)	X				
Methiocarb (S)	X				
Methyl Bromide (G)	X	X	X	X	
Sodium Azide (S)	X				
Tetraethyl Tin (L)	X	X	X		
Trichloroacetyl Chloride (L)	X	X	X	X	X
Hydrogen Sulfide (G)	X	X	X	X	
Furan (L)	X	X	X	X	
Benzotrichloride (L)	X	X			

[a] Physical state of 70°F. S = solid. L = liquid. G = gas.

[b] The physical state of the chemical in the environment at the time of release partly determines the applicability of the mitigation technology. For example, while some materials may be solid at ambient conditions, if discharged as a five particulate emission water sprayer might still be applicable for water soluble materials.

technologies that may be applicable to releases of the various toxic chemicals discussed in this manual.

In general, techniques used to disperse or control vapor emissions should emphasize simplicity and reliability. In addition to the mitigation techniques mentioned above, physical barriers such as buildings and rows of trees will help control the vapor cloud and its movement. Additional information can be found in other volumes in this series.

Physical Barriers and Basins--

Specific types of barriers and basins include excavated basins, natural basins, earth, steel, or concrete dikes, and high impounding walls. These measures are generally used in secondary containment systems which are designed to prevent the accidental discharge of toxic material from spreading to uncontrolled areas. The type of containment system best suited for a particular storage tank or process unit will depend on the risk associated with an accidental release from that location. The inventory of toxic material and its proximity to other portions of the plant and to the community should be considered when selecting a secondary containment system. The secondary containment system should be able to contain spills with a minimum of damage to the facility and its surroundings and with a minimum potential for escalating the event.

Secondary containment systems for toxic chemical storage facilities commonly consist of one of the following:

- The storage tank area drains to an impoundment basin with a capacity equal to that of the largest tank served; or

- The storage tank area is surrounded by a dike, with the diked area volume equal to that of the largest tank served.

The most common type of containment system is a low-wall dike surrounding one or more storage tanks. Generally, to reduce risk no more than one tank is enclosed within a diked area. Dike heights usually range from three to twelve feet, depending on the area available to achieve the required volumetric capacity. The dike walls should be liquid-tight and able to withstand the hydrostatic pressure and temperature of a spill. Low-wall dikes may be constructed of steel or concrete. If earthen dikes are used, care must be taken to ensure that the toxic material cannot leak through the dike. Piping should be routed over dike walls, and penetrations through the walls should be avoided if possible. Vapor fences may be situated on top of the dikes to provide additional vapor containment. If more than one tank is in the diked area, the tanks should be situated on beams above the maximum liquid level attainable in the impoundment.

A low-wall dike can effectively contain the liquid portion of an accidental release and keep the liquid from entering uncontrolled areas. By preventing the liquid from spreading, the low-wall dike can reduce the surface area of the spill. Reducing the surface area reduces the rate of evaporation. The low-wall dike will partially protect the spill from wind; this can reduce the rate of evaporation. A dike with a vapor fence provides extra protection from wind and may be even more effective at reducing the rate of evaporation. While a low-wall dike reduces the effects of an evaporating liquid, it does not for a gaseous release.

A low-wall dike can also be used to surround areas where toxic solids are stored to prevent contact with uncompatible materials in the event of a liquid spill elsewhere in the facility. If materials that would react violently with the toxic material are stored within the same diked area, the dike will increase the potential for mixing the materials in the event of a simultaneous leak. A dike also limits access to the tank during a spill.

A remote impoundment basin for capture of liquid spills is well-suited where a relatively large site is available. The flow from the spill is directed to the basin by dikes and channels. For materials with a high vapor pressure and high acute toxicity, the trenches that lead to the remote basin as well as the basin itself can be covered to reduce the rate of evaporation. The spilled liquid is removed from the immediate tank area, allowing access to the tank during the spill and reducing the probability that the spilled liquid will damage the tank, piping, electrical equipment, pumps or other equipment. In addition, the covered impoundment will reduce the rate of evaporation from the spill by protecting the spill from wind or heating from sunlight.

High-wall impoundments are an alternative secondary containment system for selected situations. Circumstances that may warrant their use include limited storage site area, the need to minimize vapor generation rates, and/or a need to protect the tank from external hazards. Maximum vapor generation rates will generally be lower for a high-wall impoundment than for low-wall dikes or remote impoundments because of the reduced surface contact area. These rates can be further reduced by using insulation on the wall and floor in the annular space. High impounding walls may be constructed of steel, reinforced concrete, or prestressed concrete. A weather shield may be installed between the tank and wall with the annular space remaining open to the atmosphere. The available area surrounding the storage tank will dictate the minimum height of the wall. For high-wall impoundments, the walls may be designed with a volumetric capacity greater than that of the tank to contain the vapors. Increasing the height of the wall also raises the elevation of any released vapor.

One disadvantage of these dikes is that the high walls around a tank may hinder routine external observation. Furthermore, the closer the wall is to the tank, the more difficult it becomes to reach the tank for inspection and maintenance. As with low-wall dikes, piping should be routed over the wall if possible. The proximity of the wall to the tank may require placing the pump outside the wall, in which case the outlet (suction) line will have to pass through the wall. In such a situation, a low dike encompassing the pipe penetration and pump may be provided, or a low dike may be placed around the entire wall.

A further type of secondary containment system is one structurally integrated with the primary system that forms a vapor-tight enclosure around the primary container. Many types of arrangements are possible. A double walled tank is an example of such an enclosure. These systems may be considered where protection of the primary container and containment of vapor are of greatest concern. Drawbacks of an integrated system are the greater complexity of the structure, the difficulty of access to certain components, and the fact that complete vapor containment cannot be guaranteed for all potential events.

Flotation Devices and Foams--

Flotation devices and foams can be used to reduce the surface area of a spilled toxic liquid, thereby minimizing the amount of toxic vapor released to the environment.

Flotation Devices--Placing an impermeable flotation device over a spilled chemical is a direct, highly percent efficient method for reducing evaporation and containing toxic vapors. Deployment, however, may be difficult in all but small spills.

Although such devices are potentially effective, no systems are currently available for mitigating toxic spills. The primary deterrent to their use is the cost associated with material and dispersal equipment. Such a system would require the dispersal of a minimum of 280 particle per square foot of spill surface (6).

Foams--One approach to a toxic chemical spill is dilution with water. However, many materials are only slightly soluble in water and a large quantity would be required for dilution. Others react violently and result in increased boil-off. Still other form highly corrosive material when contacted with water. Thus, while dilution with water may be applicable for some materials, it is not applicable for all. A water-based foam, however, is another way to dilute a toxic material.

The use of foams in vapor hazard control has been demonstrated for a broad range of volatile chemicals. Unfortunately, it is difficult to accurately quantify the benefits of foam systems because the effects will vary as a function of the chemical spilled, foam type, spill size, and atmospheric conditions.

Regardless of the type of foam used, the slower the drainage rate of the foam, the better its performance will be. A slow-draining foam will collapse more slowly. The initial cost of a slow-draining foam may be higher than that of other foams, but a cost-effective system will be realized in superior performance.

Sprays and Steam Curtains--

Water sprays and steam curtains are two mitigation technologies that might be used with some toxic gases or vapors.

Water Sprays--Water spray systems are routinely used in the chemical process industries for a variety of fire protection purposes. However, they can also be used to reduce the effects of toxic and/or flammable gas or vapor releases. Theoretical studies and experimental research have shown that such sprays can be effective in aiding the dispersion and dilution of gas or vapor clouds resulting from an accidental release (7,8,9,10,11,12,13,14). However, many of the results are based on specific systems operating under a specific set of conditions. Details concerning the overall effectiveness of these systems are limited in scope.

A spray is defined as a dispersion of liquid droplets in a gas. Sprays can achieve a variety of objectives including, but not limited to, the forced dispersion and dilution of a gas or vapor, absorption of water soluble materials, containment of released vapor or gas in a particular area, or diversion away from a particular area.

The spray medium is typically applied to the vapor cloud by hand-held hoses and/or.by stationary water-spray barriers. Important factors relating to the effectiveness of spray systems are the distance of the nozzle from the point of release, the fog pattern, nozzle gallonage, pressure, and nozzle rotation. If water sprays are used to mitigate toxic vapors from a diked area containing spilled water-reactive material, care must be taken not to be direct water into the liquid itself.

The low solubility of some materials in water limits the effectiveness of spray systems in some circumstances. An alternative is to use a reactive spray system such as an ammonia-injected water spray to neutralize the release.

Steam Curtains--Steam curtains provide an alternative to water spray systems for reducing the effects of toxic and/or flammable gas or vapor releases. Steam curtains act in a manner similar to water sprays in that the primary dispersing mechanism is the dilution of the gas or vapor with air. However, steam curtains provide enhanced buoyancy to the toxic and/or flammable cloud by heating the gas or vapor passing through the steam curtain.

A steam curtain consists of a horizontal steam pipe with a row of small holes in the top, mounted near the top of a wall. When operated, a wall of steam approximately 15 to 20 feet high is produced. The steam pipe is designed so that all of the individual jets combine to form a continuous curtain of steam which entrains sufficient air to dilute the gas or vapor to below its toxic and/or flammable limit. Additionally, the steam pipe is usually divided into sections which are individually supplied with steam from a distribution main. This allows plant operators or an automated activation system to select which sections of the steam curtain will be activated in the event of a release. In practice, steam curtains are typically controlled manually.

Steam curtains were initially designed to dilute and contain heavy flammable vapors and indeed steam curtains are incorporated into several installations to prevent highly flammable materials from reaching sources of ignition in the event of an accidental release (12). In principle, steam curtains can also be useful in mitigating toxic and/or flammable vapors which are heavier than air. No commercial steam curtain installations for use in mitigating toxic releases could be found at the time this manual was prepared.

One drawback of steam curtains is that they require large quantities of steam, typically 0.15 ton/hr per foot of curtain. Thus, steam curtains must often be limited to small scale uses. In addition, where steam is not available or the supply of steam is not reliable, water spray systems may be more applicable.

2.2.4 Operation and Maintenance Practices

Quality hardware, contained mechanical equipment, and protective devices all increase plant safety; however, they must be supported by the safety policies of management and by constraints on their operation and maintenance. This section describes how management policy and training, operation, and maintenance procedures relate to the prevention of accidental toxic chemical releases. Within the chemical industry, such practices vary widely because of differences in the size and nature of the processes and because any determination of their adequacy is inherently subjective. For this reason, the following subsections focus primarily on fundamental principles and do not attempt to define specific policies and procedures.

Management Policy--

Management is a key factor in controlling of industrial hazards and preventing accidental releases. Management establishes the broad policies and procedures that influence the implementation and execution of specific hazard-control measures. These management policies and procedures must be designed to match the level of risk in the facilities where they will be used. Most organizations have a formal safety policy. Many make policy statements to the effect that safety must rank equally with other company functions such as production and sales. The effectiveness of any safety program, however, is determined by a company's commitment to its safety plan, as demonstrated throughout the management structure. Specific goals must be derived from the safety policy and supported by all levels of management. Ideally, management should establish the specific safety performance measures, provide incentives for attaining safety goals, and commit company resources to safety and hazard control. The advantages of an explicit policy are that it sets the standard by which existing programs can be judged, and it is evidence that management views safety as a significant factor.

In the context of accident prevention, management is responsible for:

- Ensuring worker competency;
- Developing and enforcing standard operating procedures;
- Adequate documentation of policy and procedures;
- Communicating and promoting feedback on safety issues;
- Identification, assessment, and control of hazards; and
- Regular plant audits and provisions for independent checks.

More discussion of the responsibilities of management will be found in the manual on Control Technologies, part of this manual series.

Operator Training--

The performance of operating personnel is a key factor in preventing accidental chemical releases. Many case studies documenting industrial incidents note the contribution of human error to accidental releases (2). Release incidents may be caused by improper routine operating procedures, by insufficient knowledge of process variables and equipment, by lack of knowledge about emergency or upset procedures, by failure to recognize critical situations, and in some cases by direct physical mistake (e.g., turning the wrong valve). A comprehensive operator training program can decrease the potential for accidents resulting from such causes.

Operator training can include a wide range of activities and a broad spectrum of information. Training, however, is distinguished from education in that it is specific to particular tasks. While general education is important and beneficial, it is not a substitute for specific training. The content of a specific training program depends on the type of industry, the nature of the processes used, the operational skills required, the characteristics of the plant management system, and tradition.

Some general characteristics of quality industrial training programs include:

- Establishment of good working relations between management and personnel;
- Definition of trainer responsibilities and training program goals;
- Use of documentation, classroom instruction, and field training (in some cases supplemented by simulator training); and
- Frequent supplemental training and up-to-date training materials.

In many instances, training is carried out jointly by plant managers and a training staff selected by management. In others, management is solely responsible for maintaining training programs. In either case, responsibilities should be explicitly designated to ensure that the quality and quantity of training provided is adequate. Training requirements and practices can be expected to differ between small and large companies, partly because of resource needs and availability, and partly because of differences in employee turnover.

Table 2-6 lists the aspects typically involved in the training of process operators for routine process operations.

Emergency training includes topics such as:

- Recognition of alarm signals;
- Performance of specific functions (e.g., shutdown switches);
- Use of specific equipment;
- Actions to be taken on instruction to evacuate;
- Fire fighting; and
- Rehearsal of emergency situations.

Aspects specifically addressed in safety training include (2,3):

- Hazard recognition and communication;
- Actions to be taken in particular situations;
- Available safety equipment and locations;

TABLE 2-6. ASPECTS OF TRAINING PROGRAMS FOR ROUTINE PROCESS OPERATIONS

- Process goals, economics, constraints, and priorities
- Process flow diagrams
- Unit operations
- Process reactions, thermal effects
- Control systems
- Process materials quality, yields
- Process effluents and wastes
- Plant equipment and instrumentation
- Equipment identification
- Equipment manipulation
- Operating procedures
- Equipment maintenance and cleaning
- Use of tools
- Permit systems
- Equipment failure, services failure
- Fault administration
    - Alarm monitoring
    - Fault diagnosis
    - Malfunction detection
- Communications, record keeping, reporting

Source: Reference 2

- When and how to use safety equipment;

- Use and familiarity with documentation such as
  - plant design and operating manuals,
  - company safety rules and procedures,
  - procedures relevant to fire, explosion, accident, and health hazards,
  - chemical property and handling information; and

- First aid and CPR.

Although emergency and safety programs typically focus on incidents such as fires, explosions, and personnel safety, it is important that prevention of accidental chemical releases and release responses be addressed as part of these programs.

Much of the type of training discussed above is also important for management personnel. Safety training gives management the perspective necessary to formulate good policies and procedures, and to make changes that will improve the quality of plant safety programs. Lees suggests that training programs applied to managers include or define the following (2):

- Overview of technical aspects of safety and loss prevention approach;

- Company systems and procedures;

- Division of labor between safety personnel and managers with respect to training; and

- Familiarity with documented materials used by workers.

Maintenance and Modification Practices--

Plant maintenance is necessary to ensure the structural integrity of chemical processing equipment; modifications are often necessary to allow more effective production. However, since these activities are also a primary source of accidental release incidents, proper maintenance and modification practices are an important part of accidental release prevention. Use of a formal system of controls is perhaps the most effective way of ensuring that maintenance and modification are conducted safely. In many cases, control systems have had a marked effect on the level of failures experienced (2).

Permit systems and up-to-date maintenance procedures minimize the potential for accidents during maintenance operations. Permit-to-work systems control maintenance activities by specifying the work to be done, defining individual responsibilities, eliminating or protecting against hazards, and ensuring that appropriate inspection and testing procedures are followed.

Maintenance permits originate with the operating staff. Permits may be issued in one or two stages. In one-stage systems, the operations supervisor issues permits to the maintenance supervisor, who is then responsible for his staff. Two-stage systems involves a second permit issued by the maintenance supervisor to his workforce (2).

Another form of maintenance control is the maintenance information system. Ideally, these systems should log the entire maintenance history of equipment, including preventative maintenance, inspection and testing, routine servicing, and breakdown or failure maintenance. This type of system is also used to track incidents caused by factors such as human error, leaks, and fires, including identification and quantification of failures responsible for hazardous conditions, failures responsible for downtime, and failures responsible for direct repair costs.

Accidental releases are frequently the result of some aspect of plant modification. Accidents result when equipment integrity and operation are not properly assessed following modification, or when modifications are made without updating corresponding operation and maintenance instructions. In these situations, it is important that careful assessment of the modification results be of equal priority to setting the plant on-line.

For effective modification control, there must be established procedures for authorization, work activities, inspection, and assessment, complete documentation of changes, including the updating of manuals, and additional training to familiarize operators with new equipment and procedures, (2,3).

Formal procedures and checks on maintenance and modification practices must be established to ensure that such practices enhance rather than adversely affect plant safety. As with other plant practices, procedure development and complete documentation are necessary. However, training, attitude, and the degree to which the procedures are followed also significantly influence plant safety and release prevention.

The use and availability of clearly defined procedures collected in maintenance and operating manuals is crucial for preventing accidental releases. Well-written instructions should give enough information about a process that the worker with hands-on responsibility for operating or maintaining the process can do so safely, effectively, and economically. These instructions not only document the path to the desired results, but also are the basis for most industrial training programs (2,3). In the chemical industry, operating and maintenance manuals vary in content and detail. To some extent, this variation is a function of process type and complexity; however, in many cases it is a function of management policy. Because of their importance to the safe operation of a chemical process, these manuals must be as clear, straightforward, and as complete as possible. In addition, standard procedures should be developed and documented before plant startup, and appropriate revisions should be made throughout plant operations.

Operation and maintenance may be combined or documented separately. Procedures should include startup, shutdown, hazard identification, upset conditions, emergency situations, inspection and testing, and modifications (2). Several authors think industrial plant operating manuals should include (2,3,15,16):

- Process descriptions;
- A comprehensive safety and occupational health section;
- Information regarding environmental controls;
- Detailed operating instructions, including startup and shutdown procedures;
- Upset and emergency procedures;
- Sampling instructions;
- Operating documents (e.g., logs, standard calculations);
- Procedures related to hazard identification;
- Information regarding safety equipment;
- Descriptions of job responsibilities; and
- Reference materials.

Plant maintenance manuals typically contain procedures not only for routine maintenance, but also for inspection and testing, preventive maintenance, and plant or process modifications. These procedures include specific items such as codes and supporting documentation for maintenance and modifications such as codes and supporting documentation for maintenance and modifications (e.g., permits to work, clearance certificates), equipment identification and location guides, inspection and lubrication schedules, information on lubricants, gaskets, valve packings and seals, maintenance stock requirements, standard repair times, equipment turnaround schedules, and specific inspection codes (e.g., for vessels and pressure systems) (2). Full documentation of the maintenance required for protective devices is a particularly important aspect of formal maintenance systems.

The preparation of operating and maintenance manuals, their availability, and the familiarity of workers with their contents are all important to safe plant operations. The objective, however, is to maintain this safe practice throughout the life of the plant. Therefore, as processes and conditions are modified, documented procedures must also be modified.

2.2.5 Control Effectiveness

It is difficult to quantify the control effectiveness of preventive and protective measures to reduce the probability and magnitude of accidental releases. Preventive measures, which may involve numerous combinations of process design, and operational measures, are especially difficult to quantify because they reduce the probability of a release rather than a physical quantity of chemical. Protective measures are more analogous to traditional pollution control technologies. Thus they may be easier to quantify in terms of their efficiency in reducing the quantity of released chemical.

Preventive measures reduce the probability of an accidental release by increasing the reliability of process systems operations and equipment. Control effectiveness can thus be expressed for both the qualitative and quantitative improvements achieved. Table 2-7 summarizes what appear to be major design, equipment, and operational measures applicable to the some primary hazards identified for various toxic chemical applications in the U.S. The items listed in Table 2-7 are for illustration only and do not necessarily

TABLE 2-7. EXAMPLES OF MAJOR PREVENTION AND PROTECTION MEASURES FOR TOXIC CHEMICAL RELEASES

Process Hazard	Prevention/Protection[1]
External fire	Water sprays to cool exposed chemical storage vessels; siting away from flammables; refrigeration systems; heat shield.
Flexible connection failures	Minimize use; higher quality components; operator training in proper assembly.
Fusible plug failure	Inspection/certification; storage in a containment building.
Human error	Increased training and supervision; use of automatic systems.
Container failure	Adequate pressure relief; inspection and maintenance; corrosion monitoring; siting away from fire and mechanical damage.
Vehicular collisions	Location; physical barriers; warning signs; training.
Water intrusion	Pad gas drying; backflow prevention; equipment purging with dry gas.
Excess flow rates	Enhanced flow control; limited over-design of feed systems; fail-shut control valves.
Temperature control of reactor	Redundant temperature sensing and alarms; interlocked feed shut-off.
Heating media flow control	Enhanced flow control; redundant temperature sensing and alarms.
Cooling media flow control	Enhanced flow control; redundant temperature sensing and alarms.
Direct relief discharges to atmosphere	Emergency scrubber system; tank enclosures.

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[1] Includes controls, monitors, design, layout, and training.

(Continued)

TABLE 2-7. (Continued)

Process Hazard	Prevention/Protection[1]
Major tank or line rupture	Diking; enclosure with scrubber; corrosion monitoring; overpressure protection; siting away from flammables and mechanical damage; inspection and non-destructive testing; foams; water sprays.
Failure of mixing	Interlock feed shut-off on loss of mixing power.
Overfilling	Redundant level sensing, alarms and interlocks; training of operators.
Overpressure	Redundant pressure relief; not isolatable; adequate size; discharge not restricted.
Corrosion	Increased monitoring with more frequent inspections; use of pH sensing on cooling water and steam condensate loops; use of corrosion coupons; visual inspections; non-destructive testing.

[1] Includes controls, monitors design, layout, and training.

represent a satisfactory option for all cases. These control options appear to reduce the risk associated with an accidental release when viewed from a broad perspective. However, there are undoubtedly specific cases where these control options will not be appropriate. Each case must be evaluated individually.

2.2.6 Estimating Costs of Release Prevention, Protection, and Mitigation

Prevention and Protection Measures--

Preventive measures reduce the probability of an accidental release from a process or storage facility by increasing the reliability of both process systems operations and equipment. Along with an increase in the reliability of a system is an increase in the capital and annual costs associated with incorporating prevention and protection measures into a system. Costs associated with increased reliability for prevention measures are not always easy to determine because of complex interactions between design, construction, operation, and maintenance decisions concerning such measures. Allocation of costs specifically to release prevention are not always readily separated from costs for enhancing process operability or other improvements.

Costs for protection measures such as flares or scrubbers are easier to determine since they are clearly add-ons to a basic process system.

For both categories of control measures, and for mitigation also, there can be varying degrees of probability (prevention and protection) and consequences reduction (mitigation) related to how many and what types of control measures are part of a system. The concept of "Levels of Control" emerges.

Levels of Control--

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices as they apply to the design, construction, operation, and maintenance of facilities where hazardous chemicals are used and stored. Inherent in determining the degree to which these practices are carried out is their cost. At a minimum, equipment and procedures should be in accordance with applicable codes, standards, and regulations; however, additional protection measures can be applied.

The levels of control concept is one way of assigning costs to increased levels of prevention and protection. The minimum level is referred to as the "Baseline" system. This system consists of the elements required for normal safe operation and for basic prevention of an accidental hazardous release.

The second level of control is "Level 1", which includes the baseline system plus modifications such as improved materials of construction, additional controls, and generally more extensive release prevention measures. The costs associated with this level are higher than the baseline system costs.

The third level of control is "Level 2", which incorporates both the "Baseline" and "Level 1" systems plus additional modifications such as alarm and interlock systems designed specifically for the prevention of an accidental release. The extra accidental release prevention measures incorporated into "Level 2" are reflected in its cost, which is much higher than that of the baseline system.

At the present time there are not universally accepted levels of control; these levels are relative attributes of a system or facility only.

When comparing the costs of the various levels of control, it is important to realize that higher costs do not necessarily imply improved safety. The measures must be applied correctly. Inappropriate modifications or add-ons may not make a system safer. Each added control option increases the complexity of a system. In some cases, the hazards associated with the increased complexity may outweigh the benefits derived from the particular control option. Proper design and construction and proper operational practices are needed to ensure safe operation.

Some examples were developed for which cost estimates were prepared to provide some indication of how control costs might vary by level. Various possible control measures applied to a generic "typical" storage tank system are presented in Table 2-8. An actual system is likely to incorporate some items from each of the levels of control.

A summary of cost estimates for the tank at the different control levels is presented in Table 2-9. From the table it can be seen that significant cost differences can occur from different levels of control. Selection of an appropriate control level would involve an evaluation of the cost effectiveness or how much probability and consequences reduction could be achieved for each cost increment of additional controls. Further examination of this topic is beyond the scope of this study. The example is provided only to make the user aware that there can be varying economic implications of various levels of release prevention in a manner analogous to pollution controls.

TABLE 2-8. EXAMPLE OF LEVELS OF CONTROL FOR GENERIC TOXIC CHEMICAL STORAGE TANK[a]

Process: Fixed storage tank
10,000 gal capacity

Controls	Baseline	Level No. 1	Level No. 2
Flow:	Single check-valve on tank-process feed line	Add second check valve.	Add a reduced-pressure device[b] with internal air gap and relief vent to scrubber.
Temperature:	Temperature indicator and alarm.	Add remote indicator	Add redundant sensors and alarms.
Pressure:	Single pressure relief valve, vent to atmosphere, provide local pressure indicator.	Add second relief valve, secure non-isolatable installation; vent to scrubber.	Add rupture disks under relief valves; provide local pressure indication on space between disk and valves; vent to scrubber.
Quantity:	Local level indicator and alarm.	Add remote level indicator.	Add level alarm. Add high-low level interlock shut-off for both inlet and outlet lines.
Location:	Away from traffic, flammables, and other hazardous processes.	Same	Same
Materials of Construction:	Carbon steel.	Carbon steel with increased corrosion allowances. (1/8 inch)	Monel®
Vessel:	Tank pressure specification 225 psig.	Tank pressure specification 300 psig.	Tank pressure specification 375 psig.

(Continued)

TABLE 2-8 (Continued)

Process: Fixed storage tank
10,000 gal capacity

Controls	Baseline	Level No. 1	Level No. 2
Piping:	Sch. 40 carbon steel	Sch. 80 carbon steel.	Sch. 80 Monel®.
Process Machinery:	Centrifugal pump, carbon steel, stuffing box seal.	Centrifugal pump, Monel® double mechanical seal.	Magnetically-coupled centrifugal pump Monel®.
Enclosures:	None	None	Steel building.
Diking:	3 ft high dike.	3 ft. high dike.	Top of tank height, 10 ft.
Scrubbers:	None	Water scrubber for relief and building vents.	Alkaline scrubber for relief and building vents.
Mitigation:	None	Water sprays.	Alkaline water sprays and barriers.

[a] The examples in this table are appropriate for many, but not all applications. This is only an example system. The design must be suited to fit the specific service.

[b] A reduced pressure device is a modified double check valve.

TABLE 2-9. SUMMARY COST ESTIMATES OF POTENTIAL LEVELS OF CONTROLS FOR TOXIC CHEMICAL STORAGE TANK

	Level of Control	Total Capital Cost (1986 $)	Total Annual Cost (1986 $/yr)
Storage Tank; Fixed Tank with 10,000 Gallon Capacity	Baseline	210,000	25,000
	Level No. 1	506,000	60,000
	Level No. 2	767,000	91,000

SECTION 3

INDIVIDUAL CHEMICAL SUMMARIES

This section examines the specific hazards associated with the manufacture, use, and storage of 13 toxic chemicals selected from the SARA Section 302(a) list of "extremely hazardous substances." Chemicals discussed in this section are: acrylonitrile, benzenearsonic acid, benzotrichloride, chloroacetic acid, furan, hydrazine, hydrogen sulfide, mechlorethamine, methiocarb, methyl bromide, sodium azide, tetraethyl tin, and trichloroacetyl chloride. Physical properties, chemical properties, toxicological and health effects, manufacturing processes, and hazards during manufacturing, use, and storage are presented for each chemical. Each chemical summary is an overview of major characteristics of each chemical and its processes that have a bearing on accidental releases. Most of the chemicals can be manufactured by more than one process, and have multiple uses also involving numerous processes. Scope limitations for this study precluded examination of all processes, but the basic principles discussed in Section 2 as well as the chemical specific examples given here should be sufficient for a qualified individual to extend these principles to new situations that might be encountered. A table, showing examples of potential hazard locations, hazardous conditions, and process controls which can be used to reduce the hazard is presented for each chemical.

The individual chemical summaries of this section are to be used in conjunction with Section 2 of this manual for the evaluation of a facility manufacturing, using or storing one of the 13 chemicals. The information in Section 2 was presented there in order to minimize repetition in each chemical summary of generic considerations for release prevention, protection, and mitigation.

3.1 ACRYLONITRILE

Acrylonitrile is an important chemical raw material in the plastics industry. It is used primarily to manufacture fibers, but also resins, elastomers, and intermediates for other polymeric materials.

All current U.S. manufacture of acrylonitrile is based on the Sohio ammonidation process. In 1983, 2,146 million pounds of acrylonitrile were manufactured at five sites ranging in capacity from 300 to 460 million pounds per year (17). At that time, the projected demand for 1987 was 1,590 million pounds (18).

3.1.1 Chemical Characteristics

Physical Properties and Hazards--

Arcylonitrile is a colorless liquid at common room temperatures (65-75°F) with a characteristic odor described sometimes as similar to peach seeds. Table 3-1 lists the physical properties of acrylonitrile. Acrylonitrile is soluble in water up to 7.3% by weight at 68°F (19). It is miscible with numerous solvents including acetone, benzene, carbon tetrachloride, toluene, diethyl ether, ethyl acetate, and methanol. Acrylonitrile vapor is more dense than air at the same temperature and will tend to stay close to the ground when released to the atmosphere. Liquid acrylonitrile expands slightly with heating. Liquid-full equipment with little or no vapor space above the liquid poses a containment failure hazard from thermal expansion of the liquid.

Chemical Properties and Hazards--

Acrylonitrile is a relatively reactive chemical because of both an unsaturated carbon bond and an active nitrile group in the molecule. The most striking chemical characteristic of acrylonitrile is its ability to spontaneously polymerize in storage. Commercial acrylonitrile usually contains polymerization inhibitors.

TABLE 3-1. PHYSICAL PROPERTIES OF ACRYLONITRILE

		Reference
CAS Registry Number	107-13-1	
Chemical Formula	C_3H_3N	
Odor	faintly pungent	19
Molecular Weight	53.06	
Normal Boiling Point	171.14 °F @ 14.7 psia	20
Melting Point	-118.4 °F	20
Liquid Specific Gravity (H_2O=1)	0.807 @ 68 °F	19
Vapor Specific Gravity (air=1)	1.83	19
Vapor Pressure	1.75 psia @ 68 °F	21
Vapor Pressure Equation[a]:		21

$$\text{Log}\ \ Pv = A - \frac{B}{T+C}\ .$$

Where: Pv = vapor pressure, mm Hg
T = temperature, °C
A = 7.03855, a constant
B = 1,232.53, a constant
C = 222.47, a constant

Liquid Viscosity	0.34 centipoise @ 77 °F	19
Solubility in Water	7.3% by weight	19
Specific Heat at Constant Pressure	0.50 Btu/(lb-°F)	19
Latent Heat of Vaporization	262 Btu/lb	21
Liquid Surface Tension	27.3 dynes/cm @ 75.2 °F	20
Heat of Combustion	759,000 Btu/lbmole	20
Autoignition Temperature	898 °F	20

(Continued)

TABLE 3-1 (Continued)

		Reference
Explosive Range, Volume % in air @ 1 atm and 77 °F	2.6 min. 17.5 max.	22
Flashpoint, TCC (ASTM D-56)	32 °F	22
Properties useful in determining other properties from physical property correlations.		
Critical Temperature	475 °F	20
Critical Pressure	513 psia	20
Critical Density	16.44 lb/ft^3	19

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[a] This equation yields a vapor pressure of 16.3 psia rather than 14.7 psia at the boiling point. No explanation of this discrepancy was provided in the reference for vapor pressure but may be due to curve fit averaging of experimental data.

Chemical characteristics of acrylonitrile that could contribute to an accidental release hazard include:

- Flammability - Acrylonitrile ignites readily and can form explosive mixtures in air at concentrations from 2.6 to 17.5 percent by volume of acrylonitrile.
- Polymerization - Pure acrylonitrile can undergo spontaneous polymerization, especially in the absence of oxygen or on exposure to light. The self-polymerization reaction is exothermic and the heat released will promote further polymerization. The polymerization reaction occurs violently in the presence of strong bases.
- Formation of toxic combustion products - When acrylonitrile is heated or burned, highly toxic hydrogen cyanide gas and nitrogen oxides are formed.

Acrylonitrile is reported to be especially reactive when exposed to strong acids, amines, alkalis, strong oxidizers, copper, and copper alloys (23).

Toxicological and Health Effects--

Acrylonitrile is highly toxic and may be fatal by ingestion, inhalation, and skin absorption. The Occupational Safety and Health Administration (OSHA) regulates acrylonitrile as a carcinogen, and proper use of acrylonitrile must be in conformance with Sec. 1045, Part 1910 of Title 29 of the Code of Federal Regulations. Appendices to these regulations detail recommended safety equipment and procedures. Acute acrylonitrile poisoning results in symptoms similar to cyanide poisoning, which include: irritation of the eyes and nose, limb weakness, breathing difficulty, dizziness, impaired judgement, nausea, collapse, irregular breathing, convulsions, and possible death by cardiac arrest. Prolonged exposure can result in collapse, irregular breathing, convulsions and death as a result of tissue anoxia (lack of oxygen) and cardiac arrest. The IDLH (immediate danger to life and health) concentration for acrylonitrile is 4,000 ppm. The oral lethal dose for humans is approximately 50-500 mg/kg (between 1 teaspoon and 1 ounces) for a 150 pound person) (24). The LD_{50} for rats via ingestion is 78 mg/kg (25). Table 3-2 summarizes of some additional exposure limits for acrylonitrile.

3.1.2 Facility Descriptions

This subsection briefly describes the manufacture and uses of acrylonitrile in the United States. Major process hazards associated with accidental releases are discussed in Section 3.1.4.

Acrylonitrile Manufacture--

All of the acrylonitrile in the United States is manufactured by the Sohio process. Other processes used worldwide resemble the Sohio process in their basic configuration.

The Sohio process uses the vapor-phase catalytic air oxidation of propylene and ammonia in a fluidized bed. Figure 3-1 illustrates a typical manufacturing process. A mixture of ammonia, propylene, and air are fed in stoichiometric amounts to a reactor operating at 750-900 °F and 1 to 3 atmospheres of pressure (19). The residence time is usually a few seconds. The reaction typically yields about 0.8 pounds of acrylonitrile per pound of propylene fed. Acetonitrile and hydrogen cyanide are by-products (19). (These are also toxic chemicals.) The heat of reaction is recovered as steam.

The product stream from the reactor is sent to a countercurrent absorber. Water in the absorber cools and scrubs acrylonitrile and byproducts from the product stream, leaving a nitrogen off-gas which is vented from the absorber.

The aqueous stream from the absorber is fed to a recovery column. The column removes acetonitrile and water by extractive distillation and sends the acrylonitrile-hydrogen cyanide stream overhead to the lights column. The acetonitrile is removed from the water in the acetonitrile fractionator. Crude hydrogen cyanide is removed from the crude acrylonitrile as the overhead

TABLE 3-2. EXPOSURE LIMITS FOR ACRYLONITRILE

Limit	Concentration (ppm)	Description	Reference
IDLH	4,000	The concentration defined as posing an immediate danger to life and health (i.e. causes irreversible toxic effects for a 30-minute exposure).	23
PEL	2	A time-weighted 8-hour exposure to this concentration, as set by the Occupational Safety and Health Administration (OSHA), should result in no adverse effects for the average worker.	23
TC_{LO}	16	This concentration is the lowest published concentration causing toxic effects (irritation) for a 20-minute exposure.	20
LC_{LO}	570	This concentration is the lowest published lethal concentration for a human over a 1-hour exposure.	20

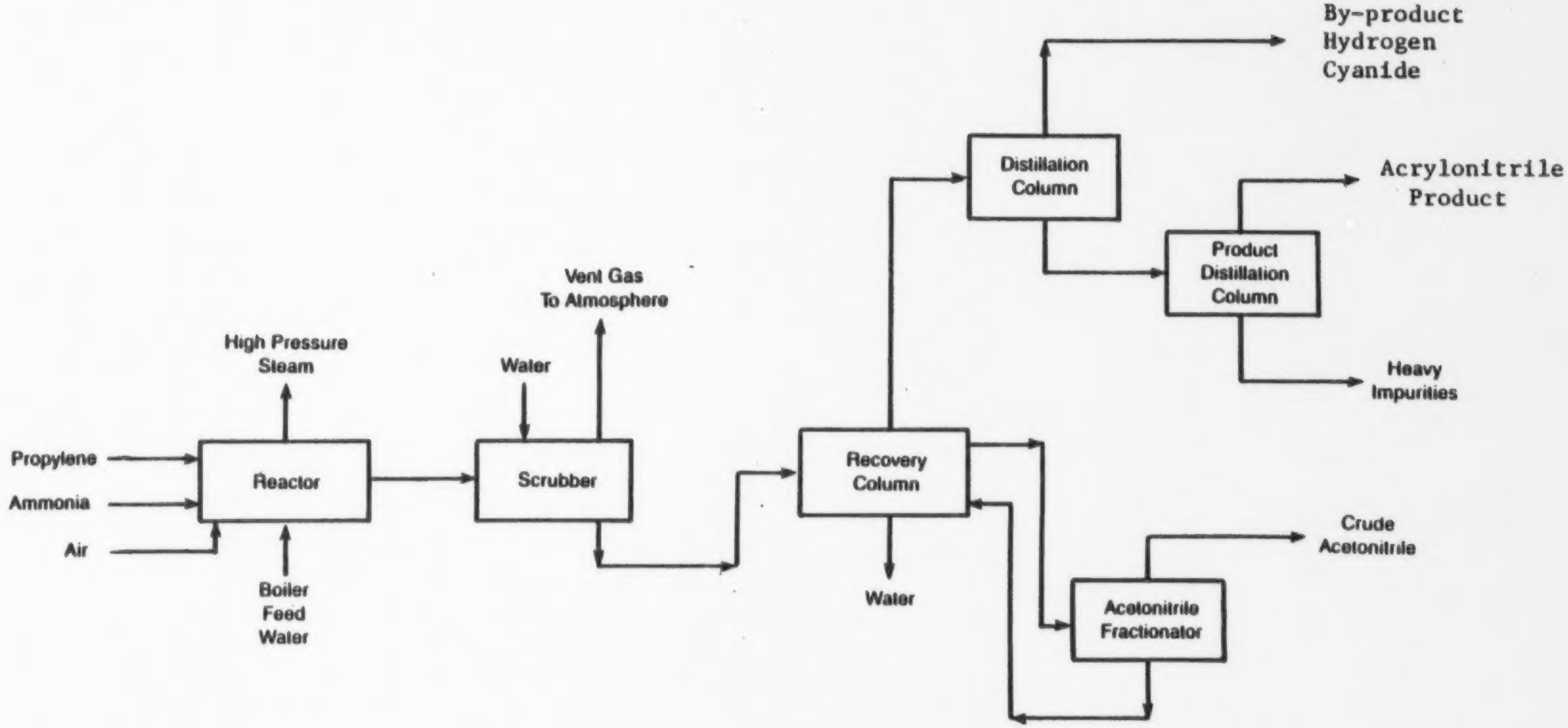

Figure 3-1. Conceptual flow diagram of Sohio acrylonitrile manufacturing process.

Adapted from: Reference 19

in the lights column. The crude acrylonitrile bottoms is sent to the product column where purified acrylonitrile is recovered as the overhead. A heavy impurities stream is sent to waste.

By-products such as hydrogen cyanide and acetonitrile are sometimes incinerated after recovery if there is a commercial oversupply of these chemicals. Excess ammonia is vented or may be converted to ammonium sulfate for disposal. Aqueous wastes containing cyanides and sulfates are often disposed of by incineration or deepwell injection.

Acrylonitrile Consumption--

The major use of acrylonitrile in the United States is for the manufacture of acrylic fibers, which accounts for about half of the U.S. consumption. Table 3-3 presents a breakdown of typical end uses of acrylonitrile.

TABLE 3-3. ESTIMATED END USE PATTERN OF ACRYLONITRILE

End Use	Percent
Acrylic Fibers	51
ABS/SAN Resins	18
Adiponitrile	14
Acrylamide	5
Nitrile Elastomers	3
Other	9

Source: Reference 18

Release hazards exist with each of the end-use processes just as they do with the fundamental manufacturing processes.

Acrylic Fibers--In fiber production, acrylonitrile is polymerized by three processes: aqueous heterogeneous polymerization, solution polymerization, and mass or bulk polymerization. A typical aqueous heterogenous polymerization process is shown in Figure 3-2. In this process, acrylonitrile monomer, water and an initiator are fed to a continuously stirred overflow reactor that operates at one atmosphere and 85-160 °F (19). A separation process removes the polymer from the mixture before it is spun into fiber.

Solution polymerization is similar to aqueous heterogenous polymerization except it eliminates the separation step by producing a polymer suitable for wet or dry spinning. Solvents used include dimethyl formamide and dimethyl sulfoxide.

Mass or bulk polymerization is also used to prepare acrylic polymers. The rate of polymerization is carefully controlled so that an easily stirred solution is maintained, thus preventing overheating that may lead to potentially explosive auto-catalytic polymerization.

ABS Resins--ABS resins are produced using emulsion, suspension, or bulk processes. Emulsion and suspension processes have historically been the dominant routes for ABS resins. However, bulk processes are also used.

A typical emulsion process is illustrated in Figure 3-3. In this process, a batch reactor operating at 40-160 °F produces a polybutadiene latex. In the next two reactors, styrene and acrylonitrile are grafted onto the polybutadiene latex as a styrene-acrylonitrile (SAN) copolymer. The grafted polymer may be blended with emulsion SAN copolymer to produce an ABS resin with the desired rubber content. The emulsion resins are recovered by coagulation procedures.

The suspension process differs from the emulsion process in that it starts with a "pre-poly" step in which lightly linked polybutadiene rubber is dissolved in monomers to produce a solution free of cross-linked rubber gels.

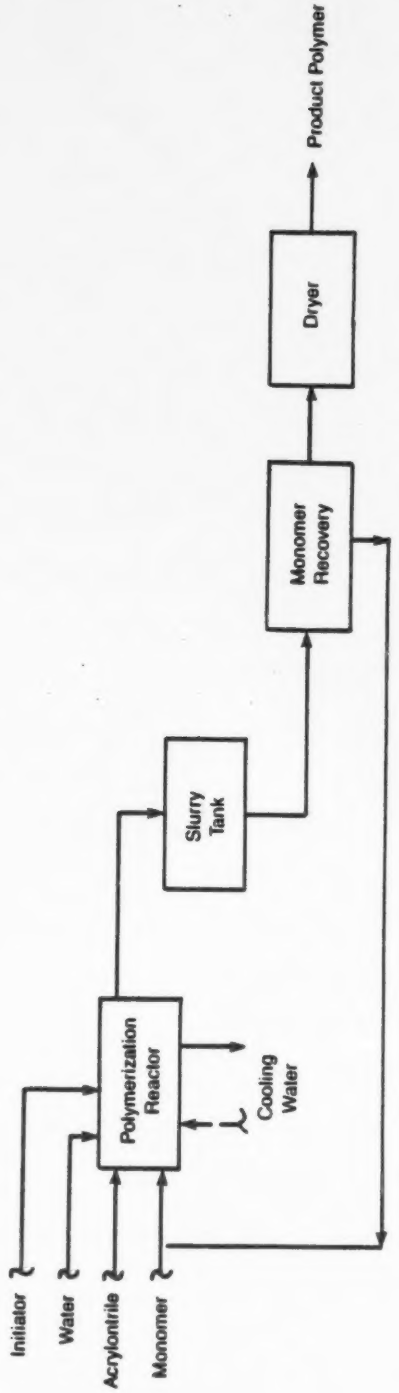

Figure 3-2. Conceptual flow diagram of typical acrylic fiber manufacturing process.

Adapted from: Reference 19

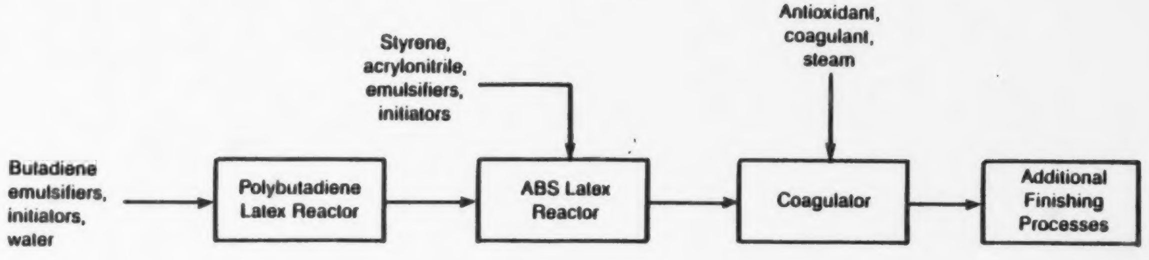

Figure 3-3. Conceptual flow diagram of typical emulsion acrylonitrile-butadiene-styrene (ABS) resin manufacturing process.

Adapted from: Reference 19

Figure 3-4 illustrates a typical suspension process. After some mass polymerization (converting 25-35 percent of monomer to polymer) and phase inversion have taken place, the polymer syrup goes to a suspension reactor, where it is dispersed in water and agitated. When the batch is complete, it is cooled and dewatered.

The bulk process consists of similar "pre-poly" and reactor steps. The polymer syrup is pumped into a specially designed bulk polymerizer operating at 250-350°F (19). The residence time may be one to five hours. After polymerization, the polymer goes to the devolatilizer, where unreacted monomer is removed and recycled. The bulk process does not require dewatering, which saves energy and avoids the need for wastewater treatment.

SAN Resins--SAN resins are produced by emulsion, suspension, or continuous mass processes similar to those used in ABS resin production. The emulsion process produces SAN copolymers in a batch or continuous reactor system from a mixture of initiator-emulsifier and monomer solutions. The copolymer is recovered by coagulation of the emulsion latex.

The suspension process for SAN resins does not contain the "pre-poly" step, but otherwise it is similar to that for the ABS resins. The reaction system contains monomers, chain-transfer agents, initiators, suspending agents, and water. It produces a small polymer sphere, and the mixture is centrifuged during dewatering.

In the continuous mass process, the feed goes to a screw reactor, where the reaction is initiated thermally or catalytically. The highly viscous polymeric melt has impurities removed in a devolatilizer. Instead of a screw reactor, a stirred tank reactor may be used, but the high viscosity of the mixture can be a problem. One option for handling the mixture would be adding a solvent that could be removed in the devolatilizer. Although the viscous mixture is a problem, an advantage of the continuous mass process is that it is self-contained because it requires no wastewater treatment and minimizes other environmental effects. From an accidental release perspective, the

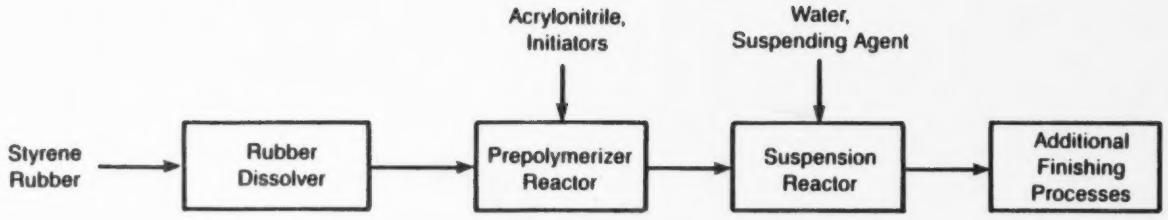

Figure 3-4. Conceptual flow diagram of typical suspension acrylonitrile-butadiene-styrene (ABS) manufacturing process.

Adapted from: Reference 19

smaller inventory of in-process material in a screw reactor appears to be advantageous, but temperature control with viscous materials can sometimes be troublesome. The relative risks for acrylonitrile releases associated with the different types of reactors depends also on the relative quantities of acrylonitrile required in the respective systems.

ABS and SAN resins are used to make components for automobiles, recreational vehicles, pipe fittings, appliances, instrument panels, instrument lenses, houseware items, packaging, business machines, and telephones.

Nitrile Elastomers--Nitrile elastomer (nitrile rubber) is manufactured by emulsion polymerization techniques. Both batch or continuous processes are used. In the batch process, measured amounts of reaction ingredients are charged to an agitated, pressurized autoclave. The temperature is controlled by cooling water circulating through a jacket or internal coils. The reaction time is typically 5 to 12 hours, depending on the system (19). At the end of the reaction time, an inhibitor is added to the reaction vessel to stop the reaction, which is then transferred to a stripper to remove unreacted acrylonitrile. The continuous process is similar except a series of stirred tank reactors are used to carry out the reaction.

Acrylamide--Acrylamide is manufactured by the catalytic hydrolysis of acrylonitrile. In a typical process, an aqueous solution of acrylonitrile and water is passed at 70-400 °F through a fixed bed catalytic reactor (19). The reactor products, containing acrylamide and unreacted acrylonitrile, are sent to a stripping column. Acrylonitrile and some water in the overhead are recycled to the reactor. Acrylamide is used in paper manufacturing, waste treatment, and some mining applications.

Adiponitrile--Adiponitrile is manufactured principally to use as an intermediate in the production of hexamethylenediamine. One adiponitrile manufacturing process involves the dimerization of acrylonitrile. In electrolytic cell, a mixture of acrylonitrile, water, and tetralkylammonium salt serves as the catholyte, while sulfuric acid serves as the anolyte. A quantity of catholyte is continuously removed and adiponitrile and unreacted acrylonitrile are recovered. The acrylonitrile is recycled back to the cell. The cell typically operates at approximately 120-140 °F. The catholyte is extracted with water and acrylonitrile. The extract, containing acrylonitrile and adiponitrile, is sent to a distillation column where acrylonitrile is removed overhead. The crude adiponitrile product is redistilled to remove impurities and sent to storage.

3.1.3 Summary of Major Process Hazards and Control Technologies

For all processes, the accidental release risk can be reduced by applying specific measures broadly classified as prevention, protection or mitigation measures. The general features of these measures applicable to acrylonitrile or any toxic chemical, were summarily discussed in Section 2 of this manual, and are discussed in other technical literature.

The two most significant chemical properties of acrylonitrile that contribute to the risk of an acrylonitrile release are its ability to self polymerize and its flammability. In addition to generic prevention measures, specific measures for acrylonitrile are to prevent conditions that could lead to self-polymerization, or fires and explosions.

In the processes that use acrylonitrile, the concerns parallel those for acrylonitrile manufacture. For all of these processes, the reactor area to which acrylonitrile is fed is a high hazard area because of the potential relatively large inventory, especially if there is a feed control failure, and the exothermicity of polymerization reactions. Below is a summary of hazard areas in acrylonitrile manufacturing, use and storage processes.

Acrylonitrile Manufacturing--

The reactor and the two product distillation columns appear to be the highest hazard areas for potential accidental releases of acrylonitrile in the manufacturing process. The reactor has a low inventory of acrylonitrile;

however, the reaction is exothermic and heat must be removed. This is typically accomplished by the production of steam. A loss of water flow to the reactor could cause a loss of temperature control that could overpressure the reactor. This in turn could cause a release through a relief valve or equipment failure. The feed to the reactor includes propylene which is a highly flammable material. A loss of composition control could cause excess feed proportions of propylene and air. Flammable mixtures could be formed in the reactor and/or downstream of the reactor, which could result in a fire and/or explosion. Water leakage through heat exchanger tubes could lead to corrosion in the reactor which could lead to equipment failure and an acrylonitrile release. Reactor failures of these types could damage other portions of the process and could lead to an accidental release of acrylonitrile.

The product distillation columns are high-hazard locations because of the high inventories of acrylonitrile. Loss of temperature control could result in an overpressure of a column and a release through a relief valve or equipment failure. A loss of temperature or composition control could cause self polymerization, which could result in an overpressure, a relief discharge or equipment failure and an accidental release. Another toxic release hazard of the distillation column is hydrogen cyanide. While the scope of this section is acrylonitrile releases, this hazard is significant enough to be worthy of mention.

Acrylic Fiber Manufacturing--

The primary acrylonitrile accidental release hazard in acrylic fiber production is the potential for overheating and corresponding overpressure that could lead to a release through pressure relief or containment failure.

Overheating of a polymerization reaction could be caused by a variety of process upsets or failures. Examples include the following: a loss of adequate mixing resulting in uneven heat distribution with localized hot spots; a loss of composition control resulting in a feed that has inadequate solvent to absorb the heat of reaction and maintain the fluid level in the reactor to ensure adequate agitation; a loss of composition control resulting in an excess of initiator that could result in excessive reaction rates and heat generation; and a loss of cooling to the reactor which could also result directly in reactor overheating.

Because of their large inventories and cyclic operation, batch polymerization reactors may present a greater hazard than stirred tank, tubular, or other continuous reactors which generally have a smaller inventory for a given production rate.

ABS Resin Production--

The primary acrylonitrile release hazard for the ABS resin production process is the same as for the polymerization processes discussed above--a loss of temperature control. The potential for such a loss of control will be closely tied to the particular polymer's tendency to undergo auto-catalytic polymerization. The temperature at which such polymerization will begin, as well as the sensitivity of this reaction to impurities, depends on specific temperature and pressure operating conditions.

SAN Resin Production--

See Acrylonitrile Manufacturing.

Nitrile Elastomers--

See Acrylonitrile Manufacturing.

Acrylamide--

See Acrylonitrile Manufacturing.

Adiponitrile Production--

The release hazard area for the adiponitrile process is the electrolytic cell and acrylonitrile recovery operation. A loss of composition control could result in a high concentration of acrylonitrile, which could result in an overheating with auto-catalytic polymerization. The recovery operation is a high-hazard area because of the high concentrations of acrylonitrile. Pump or piping failures or a loss of temperature or flow control could result in an accidental release.

Table 3-4 gives examples of possible locations, conditions, and process hazards which could potentially lead to an acrylonitrile release, as well as example controls for reducing the risk of such a release. The examples are intended to be illustrative, not exhaustive. A more detailed discussion of potential causes of releases appears in other portions of the Prevention Reference Manual series.

3.1.4 Storage and Handling

In the United States, acrylonitrile is classified as a flammable liquid and poison. It can be fatal if absorbed through the skin, inhaled or ingested. Acrylonitrile vapors can form an explosive mixture with air. Thus, acrylonitrile should be stored in closed systems. Static electricity is a significant hazard which requires careful attention to equipment grounding and the use of non-sparking tools.

Table 3-5 presents a listing of materials of construction suitable for use in acrylonitrile related processes. Carbon steel is typically used for piping and storage vessels at ambient conditions (19). In more severe conditions, stainless steel is desirable. Storage tanks should be electrically grounded because of the flammability hazards with acrylonitrile. Any vent lines discharging to the atmosphere should be routed through scrubbers or vent condensers to prevent releases of toxic vapor to the atmosphere.

Because of its ability to undergo auto-catalytic polymerization, acrylonitrile storage vessels should be equipped with a number of special safety features. Some examples include:

- Continuous local and remote temperature monitors with high temperature alarms;

TABLE 3-4. EXAMPLE CONDITIONS, PROCESS HAZARDS AND HAZARD CONTROLS IN ACRYLONITRILE MANUFACTURING AND USE

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Acrylonitrile production and polymerization reactors	Loss of cooling	Excessive exothermic reaction causing overheating or overpressurization and equipment failure	Redundant temperature sensing with alarms and/or interlocks Backup emergency cooling system with redundant controls Strict high safety maintenance, and inspection procedures
	Water leakage through heat exchanger tubes	Corrosion in reactor; equipment failure and release	Proper materials of construction; increased maintenance inspection of tubes
Polymerization reactors	Inadequate mixing	Localized or general overheating and overpressurization leading to equipment failure and a release	Agitation monitoring with alarms Interlock feed with agitation Emergency cooling capacity
Acrylonitrile storage vessels, or polymerization reactors	Excess acrylonitrile	Overfilling or overpressurization leading to a release	Redundant high level alarms interlocked to feed control Strict high quality operating procedures and operator training

(Continued)

TABLE 3-4. (Continued)

Location	Condition	Process Hazard Leading to Release	Hazard Controls or Monitors
Acrylonitrile process or storage vessel	Backflow of alkaline or strongly acidic materials	Exothermic reaction; causing overheating; or overpressurization with equipment failure and release	Redundant check valves or feed tank in line between storage vessels and incompatible materials
Acrylonitrile process or storage vessel	Fire or explosion	Equipment damage causing release	Adequate fire protection and isolation of process and storage vessles from potential sources of ignition Inert the atmosphere in vessels Flammable gas monitors in large quantity storage areas
Distillation units for acrylonitrile separation and purification	Loss of condenser cooling	Overpressurization equipment failure or release through relief valve self-polymerization with exothermic reaction leading to overheating or overpressurization causing equipment failure and release	Backup temperature sensors with alarms Interlock to shut off reboiler heat if condenser cooling fails Adequate relief valve sizing

TABLE 3-5. CHEMICAL RESISTANCE OF VARIOUS METALS TO ACRYLONITRILE

Material	Average Penetration Per Year (inch/year)		Temperature (°F)
	<0.002	<0.02	
Aluminum	X		210
Brass		X	210
Bronze		X	80
Carbon Steel		X	100
Hastelloy-B®		X	200
Hastelloy-C®		X	200
Inconel®		X	200
Monel®		X	200
Nickel®		X	200
Stainless Steel 304		X	210
Stainless Steel 316		X	210
Tantalum		X	210
Titanium		X	210
Zirconium		X	200

Source: Reference 26

- An emergency cooling system, typically composed of a heat exchanger on a recirculation loop;
- An emergency stabilizer addition system[a]; and
- Where possible, dedicated inert gas and vent systems for the tank. This will help prevent cross contamination with polymerization initiating impurities.

Samples should be routinely drawn from acrylonitrile storage tanks to monitor the formation of polymer.

Specific features of acrylonitrile storage tanks, piping, and other equipment are cited by one vendor of acrylonitrile (22). These include: electrical grounding of the tanks, all welded construction, provision for scrubbers or vent condensors for vapors, and diking to contain the full contents of the tank if spilled. Piping should also be electrically grounded, and butt welded or flanged connections used for piping diameters over one inch. Pumps should be electrically grounded with explosion-proof motors. A special note on pumps is that centrifugal pumps are preferred because acrylonitrile may affect the lubricant in positive displacement pumps. Canned or covered pumps are suggested to minimize fugitive vapor emissions.

Since acrylonitrile has recognized carcinogenic or co-carcinogenic potential, acrylonitrile-resistant protective clothing should be worn when it is handled. Safety equipment typically includes full-face, self-contained respirators.

Acrylonitrile is shipped by tank cars, tank truck, barges, steel drums, and pipelines.

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[a] Acrylonitrile suppliers should be able to recommend specific inhibitors.

3.2 BENZENEARSONIC ACID

Benzenearsonic acid is reported to be an analytical reagent for tin (24). A review of several other technical literature sources revealed no other information on its uses. Other common names include phenyl arsenic acid and phenylarsonic acid (24).

3.2.1 Chemical Characteristics

Physical Properties and Hazards--

Benzenearsonic acid is a toxic, colorless, crystalline solid. It is somewhat soluble in water and alcohol. Table 3-6 lists some physical properties of benzenearsonic acid. It is a solid at ambient conditions. From an accidental release perspective, the hazard as a toxic dust, is a chief concern. As a solid, the contamination of soil is possible. Its moderate solubility in water makes water contamination also a possibility.

Chemical Properties and Hazards--

Little information is available concerning the chemical properties and reactivity of benzenearsonic acid; however, it is known that benzenearsonic acid decomposes when heated to its boiling point of 320 °F, releasing highly toxic fumes of arsenic (24). It has been reported that no information was found in the open technical literature on stability, incompatibility with other materials, hazardous polymerization potential, or special conditions to avoid (24). It is also reported that this material does not burn or burns with difficulty, and that no information was found on flash point or lower or upper explosive limits (24). This implies that even dust explosions do not appear to be likely with this material. The decomposition of this material to toxic fumes on heating, however, suggests an air toxic hazard if a facility containing this material were involved in a fire.

Toxicological and Health Effects--

Benzenearsonic acid is regarded as a deadly poison. Little information is currently available, however, on the toxicological effects of accidental

TABLE 3-6. PHYSICAL PROPERTIES OF BENZENEARSONIC ACID

		Reference
CAS Registry Number	98-05-5	
Chemical Formula	$C_6H_7AsO_3$	
Molecular Weight	202.05	
Melting Point	320 °F, decomposes	24
Specific Gravity (H_2O=1)	1.760	24
Solubility in Water	3.3 lb/100 lb H_2O @ 82 °F	24

exposure to benzenearsonic acid. The LD_{50} for rats by the oral route is 50 mg/kg (25). Since it is an arsenic compound, some of the toxicological effects of arsenic are likely for benzenearsonic acid. It is known that symptoms of arsenic poisoning do not appear immediately and may be delayed for many hours. These symptoms include a metallic taste and garlic-like odor, skin disorders, difficulty in breathing, abdominal pain, vomiting, diarrhea, dizziness, delirium, rapid heart beat, headache, and coma. Acute exposure can result in death. The Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit for arsenic (PEL) of 0.5 mg/m^3 in air (19).

3.2.2 Facility Descriptions

Benzenearsonic Acid Manufacture--

No information was found in the technical literature on the manufacture of benzenearsonic acid.

Benzenearsonic Acid Consumption--

Little information is available concerning the use of benzenearsonic acid. However, it has been reported that it is used as an analytical reagent for tin (21). From this it can be inferred that it is probably packaged, transported, and used in relatively small quantity containers.

3.2.3 Summary of Major Process Hazards and Control Technologies

The primary hazard of a significant accidental release of this material appears to be from an accidental spill during handling. During manufacture, if a crystallization or filtration step were used, it would be in these operations that the material is likely to be present in its most concentrated form. Generic equipment or operating failures of the type discussed in Section 2 of this manual would be likely causes. Controls would like-wise be generic.

3.2.4 Storage and Handling

Although no specific literature information was found on storage and handling, and direct contacts with manufacturers was explicitly prohibited in this study, appropriate procedures would be expected to be those for any toxic, solid chemical, which could be subject to decomposition to a toxic vapor or fume in a fire.

Considering its toxicity, preferred handling of this material is likely to be on a relatively small scale. As a solid it would likely be conveyed using screw type conveyors or even manual transfer. In either case an enclosed conveyance would prevent or reduce fugitive dust emissions, and any venting routed to well sealed dust collection equipment would prevent or reduce process emissions. Vent systems operating under a slight negative pressure would be preferable to positive pressure systems.

Well ventilated storage areas for bins, drums, or other containers can be provided with appropriate dust collection equipment. A special consideration is to ensure that storage areas have especially good fire protection because of the hazard of toxic fumes from thermal decomposition.

3.3 BENZOTRICHLORIDE

Benzotrichloride is an important chemical intermediate used primarily to produce another chemical intermediate, benzoyl chloride. Among other end uses, benzoyl chloride is used in the plastics industry to produce UV light absorbers and to initiate polymerization. Benzotrichloride is also used in dye manufacturing processes. It is estimated that in 1982, over seventeen thousand tons of benzotrichloride were produced in the United States (27).

3.3.1 Chemical Characteristics

Physical Properties and Hazards--

Benzotrichloride is a colorless to slightly yellow liquid at room temperature (65-75 °F). It has a pungent odor and fumes (forming hydrogen chloride vapors) when exposed to air. The physical properties of benzotrichloride are listed in Table 3-7. Benzotrichloride is not soluble in water but is soluble in most organic solvents such as benzene. Benzotrichloride has a relatively high boiling point (417 °F) and a very low vapor pressure at room temperatures (less than 0.01 psia at 68 °F), (27). Benzotrichloride vapor is nearly seven times as dense as air and will tend to stay close to the ground when released to the atmosphere.

Chemical Properties and Hazards--

The chemical properties of benzotrichloride that contribute to an accidental release hazard include:

- Flammability - Although not classified as a flammable liquid, benzotrichloride will autoignite in the presence of air near its boiling point (417 °F). This means that near ambient temperatures benzotrichloride is not likely to burn by itself, but it will fuel a hot fire.

TABLE 3-7. PHYSICAL PROPERTIES OF BENZOTRICHLORIDE

		Reference
CAS Registry Number	98-07-7	
Chemical Formula	$C_7H_5Cl_3$	
Molecular Weight	195.5	
Normal Boiling Point	417°F @ 14.7 psia	28
Melting Point	22°F	28
Liquid Specific Gravity (H_2O=1)	1.370	28
Vapor Specific Gravity (air=1)	6.8	28
Vapor Pressure Equation	$\log P_v = A - \frac{B}{T+C}$ where: P_v vapor pressure, mm Hg T = temperature, °C (45.8C - 213.5°C) A = 7.70437, a constant B = 2166.280, a constant C = 235.451, a constant	29
Solubility in Water	Insoluble (decomposes)	30
Latent Heat of Vaporization	112 Btu/lb	27
Heat of Combustion	7980 Btu/lb	30
Autoignition Temperature	412°F	30
Flashpoint (Cleveland open cup)	260°F	30

- Reactivity with water - Benzotrichloride will react with water to form benzoic acid and hydrochloric acid. The rate of hydrolization is enhanced in the presence of metals or their salts. Hydrolysis will also occur when benzotrichloride is exposed to acids or alcohols. Hydrolysis by water will occur slowly at ambient temperatures. However, the reaction is exothermic and will increase in speed as the benzotrichloride is warmed.

- Polymerization - Benzotrichloride can undergo self-polymerization when in contact with metals or certain acids. This reaction is exothermic.

- Corrosivity - Benzotrichloride is corrosive to most metals and is especially corrosive when moisture is present.

Toxicological and Health Effects--

Benzotrichloride is highly toxic by inhalation and when ingested. It is also irritating to the eyes and skin. Death can result from exposure by inhalation (31). No exposure limits have been established for benzotrichloride; however, one manufacturer has suggested an eight-hour time-weighted inhalation exposure limit of 0.25 parts per million by volume in air (31). The International Agency for Research on Cancer (IARC) has determined that there is sufficient animal evidence and limited human evidence that benzotrichloride is a carcinogen (25). The LD_{50} for rats via ingestion is 6 gm/kg (25). Table 3-8 summarizes the reported toxicity data.

3.3.2 Facility Descriptions

This subsection provides brief descriptions of the manufacture and uses of benzotrichloride in the United States. Major accidental release hazards of these processes are discussed in Section 3.3.4.

TABLE 3-8. TOXICITY DATA FOR BENZOTRICHLORIDE

Exposure	Effect
19 ppm for 2 hours	LC_{50} - lethal by inhalation for rats
8 ppm for 2 hours	LC_{50} - lethal by inhalation for mice
6 gm/kg	LD_{50} - lethal by ingestion for rats

Source: Reference 25

Benzotrichloride Manufacture--

Benzotrichloride is manufactured by the thermal or photochemical chlorination of toluene at 212 to 320 °F (33,34). This reaction may be carried out either in batches or continuously. The toluene feed must be heated to near 212 °F before chlorine is introduced. Once chlorine addition has begun, however, the reaction is exothermic and requires no additional heat to go to completion. The chlorination efficiency in batch reactors is low and requires several hours to go to completion (35). Efficiencies can be improved by using multistage continuous reactors. The reaction is catalyzed with UV light, or with a chemical catalyst such as phosphorus trichloride, or both (34).

Figure 3-5 shows a batch process for the production of benzotrichloride. This figure also shows the subsequent batch production of benzoyl chloride, which will be discussed later in this section. In this process, toluene is fed to a reactor and heated with steam to its boiling point. The steam is shut off and chlorine is added; benzotrichloride is produced. Unreacted toluene is allowed to boil and recondense into the reactor. The crude reaction product mixture is purified by distillation.

Benzotrichloride Consumption--

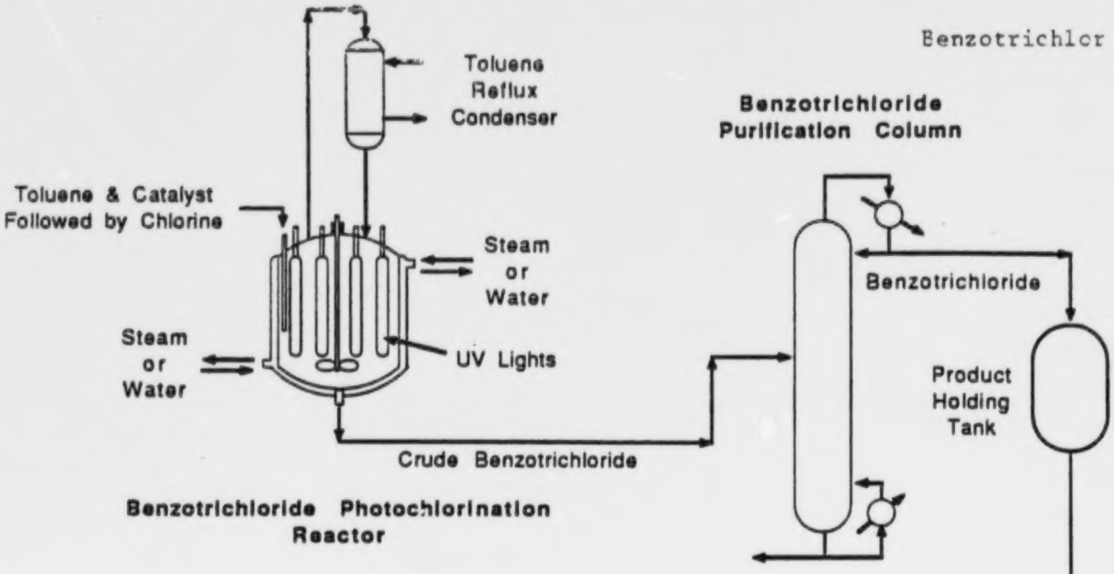
The major use of benzotrichloride is for the production of benzoyl chloride. Table 3-9 presents a breakdown of typical end uses of benzotrichloride, as well as some end uses of benzoyl chloride.

Benzoyl Chloride--Benzoyl chloride is produced by the reaction between benzotrichloride and benzoic acid. The reaction can be carried out in batches or continuously and is chemically catalyzed using, for example, zinc chloride. The reaction is carried out in the liquid phase, above the melting point of benzoic acid (about 250 °F) (35). Hydrogen chloride gas is a by-product of the reaction. The hydrogen chloride can be condensed and recovered. The crude benzoyl chloride may be purified by vacuum distillation. Figure 3-5 illustrates a batch benzoyl chloride production process downstream of a benzotrichloride batch production process.

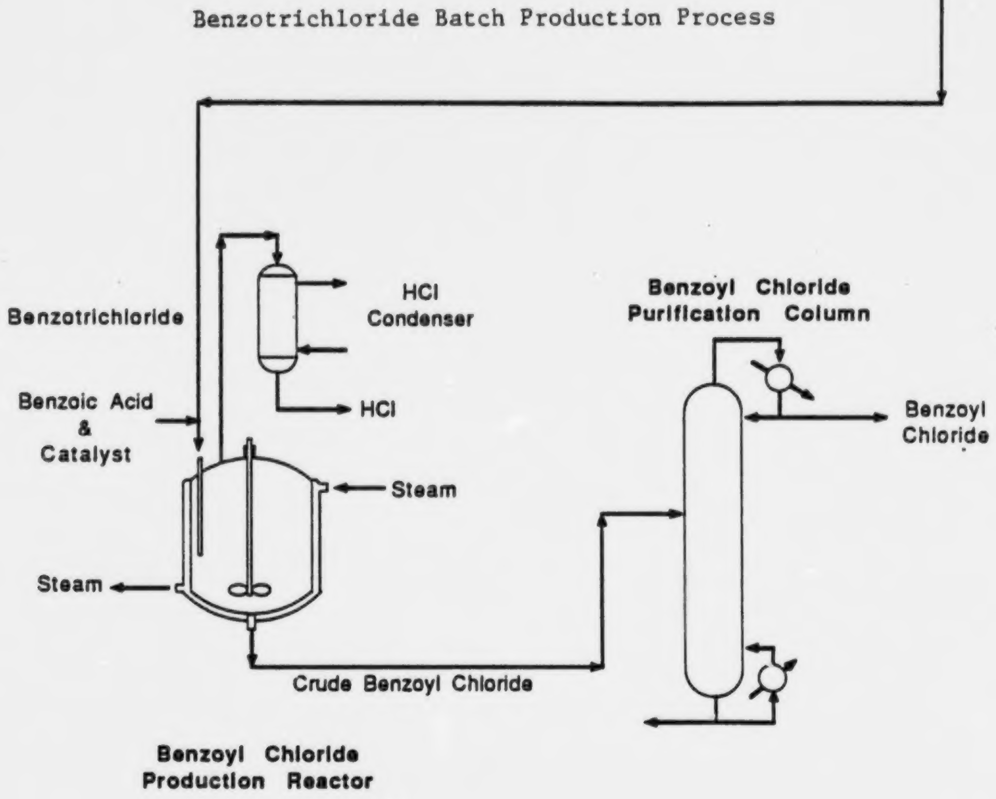
TABLE 3-9. TYPICAL USES OF BENZOTRICHLORIDE

Primary Uses
Dyes
Benzoyl Chloride
Uses of Benzoyl Chloride
Herbicides
Benzoyl Peroxide (used in plastics manufacture)
Benzophenone (used in perfumes, UV light absorbers)
Glycol Dibenzoate Plasticizers (used in plastics manufacture)

Source: Reference 36



Benzotrichloride Batch Production Process



Benzoyl Chloride Batch Production Process

Figure 3-5. Conceptual flow diagram of benzotrichloride and benzoyl chloride batch production processes.

Adapted from: Reference 35

3.3.3 Summary of Major Process Hazards and Control Technologies

To reduce the risk of an accidental release specific measures broadly classified as prevention, protection or mitigation measures may be applied. These measures are discussed generally in Section 2 and are described in detail elsewhere in the technical literature.

The properties of benzotrichloride that can promote equipment failure are its corrosivity, flammability and reactivity with water or acids. Below is a summary of hazard areas in the benzotrichloride manufacturing, use, and storage processes.

Benzotrichloride Manufacture--

The reactor and product distillation columns appear to have the highest potential for an accidental release. The final product storage vessel is also potentially the site of an accidental benzotrichloride release.

The reaction to produce benzotrichloride is exothermic. Often, the heat of reaction is removed by allowing some of the toluene to boil off and recondense. A loss of condenser cooling, however, could result in a loss of temperature control followed by a runaway reaction. The reaction between toluene and chlorine is very slow at temperatures below 140 °F. Below this temperature, chlorine is fairly soluble in toluene; therefore, feeding chlorine to toluene that has not been adequately warmed will result in an accumulation of unreacted chlorine. Once the chlorine begins to react, the solution will warm and a runaway reaction can follow (35). This runaway reaction can result in an accidental release because of reactor overpressure.

The product distillation columns are high-hazard areas because of the quantity and concentration of benzotrichloride present at elevated temperatures. A loss of condenser cooling could lead to overpressure and a benzotrichloride release. Internal corrosion could also result in vessel failure and release.

Product storage is a potential hazard area because of the large quantity of benzotrichloride; however, because of its low vapor pressure at ambient temperatures, a release of liquid benzotrichloride from an ambient temperature storage vessel is not likely to result in a serious risk of exposure to off-site locations. A source of heat would probably be required before sufficient quantities of benzotrichloride vapor could threaten off-site locations. For example, the accidental introduction of water to a storage vessel could create sufficient heat and pressure to result in a containment failure and a release of benzotrichloride vapor. Another example would be a spill of benzotrichloride into water, which could produce enough heat to evaporate some benzotrichloride before it reacted with the water.

Benzoyl Chloride Production--

The reaction feed tanks and the benzoyl chloride production reactors are the locations of greatest accidental release risk. Although this reaction is run under relatively mild conditions (250 to 270 °F and atmospheric pressures), it is conceivable that a loss of temperature control or a failure to provide adequate vent capacity for the hydrogen chloride could lead to overpressure and an accidental release of benzotrichloride.

Table 3-10 presents examples of possible locations, conditions and process hazards which could potentially lead to a benzotrichloride release, and example control options for reducing the risk of such a release. The examples are intended to be illustrative, not exhaustive.

3.3.4 Storage and Handling

The Department of Transportation classifies benzotrichloride as a corrosive liquid. The presence of moisture will enhance its corrosivity. It can be fatal if inhaled and is an irritant to the skin and eyes; therefore, it should be stored in closed systems.

TABLE 3-10. EXAMPLE CONDITIONS, PROCESS HAZARDS AND HAZARD CONTROLS IN BENZOTRICHLORIDE MANUFACTURING, USE AND STORAGE

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Reactor	Inadequate preheating of toluene feed	Chlorine accumulation, runaway reaction and overpressurization	Improved operating procedures Interlock feed temperature to chlorine feed Overpressure protection vented to a scrubber
Process or storage vessel	Undetected corrosion	Self-polymerization with overheating and possible equipment failure	Regular inspection of lining
Distillation column	Loss of cooling	Overpressurization and loss of containment	Backup cooling system Redundant temperature controls with alarms Overpressure protection vented to a scrubber Interlock to shut off reboiler heat if condenser cooling fails
Process or storage vessels	Back-flow of water or acidic materials into vessels with benzotrichloride	Exothermic hydrolysis and overpressurization	Redundant check valves or blinds in lines leading to possible contamination

(Continued)

TABLE 3-10. (Continued)

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Process or storage vessel	Transfer of benzotrichloride to steel container	Corrosion or self-polymerization	Improved operator training Piping configurations that prohibit improper transfer
Reactor used in benzoyl chloride production	Loss of temperature control	Overpressurization	Adequate vent capacity Redundant temperature sensors with alarms

The preferred materials of construction for systems handling benzotrichloride are nickel, glass, or fluoroplastics (41). However, phenolic or polyethylene linings are acceptable for storage or shipping containers. Lined equipment should be inspected regularly, since imperfections in the lining can expose the underlying metal to benzotrichloride. If the underlying metal has poor corrosion resistance to benzotrichloride (as is typical for lined equipment), then the metal will corrode. If undetected, corrosion may result in structural failure. Since most metals (apparently not nickel since it is reported as a material of construction) can catalyze self polymerization of benzotrichloride, care must be taken to ensure that benzotrichloride is never incorrectly stored in metal tanks. Fittings on storage vessels should be constructed of materials compatible with benzotrichloride. The addition of a polymerization inhibitor is usually not required for benzotrichloride storage; however, benzotrichloride stored for weeks at a time should be sampled periodically for changes in color. A change in color (darkening) can indicate that polymerization and/or internal tank corrosion is occurring.

Benzotrichloride storage vessels should be grounded and diked. Vents from storage or process vessels should be routed to an alkaline scrubber (such as sodium hydroxide) or to an incinerator.

Storage and Handling--

Extreme caution should be taken to ensure that water or acids are not allowed to enter vessels containing benzotrichloride. The resulting reaction is exothermic and can produce two moles of hydrogen chloride vapor per mole of water introduced. This combination of heat generation and gas evolution could lead to a substantial pressure rise in the vessel, followed by containment failure and accidental release. Precautions to prevent water or acid contamination could include blinds in all water lines that connect to the process, redundant check valves in lines that connect the vessel to potential sources of contamination, or stringent drying procedures whenever a tank is washed with water.

Spills of benzotrichloride should either be pumped back into a storage vessel or absorbed onto clay or some other absorbing medium. Water should never be added to a benzotrichloride spill since the heat of reaction will only exacerbate the rate of vapor generation.

Benzotrichloride is shipped in fifty-five-gallon drums and four thousand-gallon tank trailers (41).

3.4 CHLOROACETIC ACID

Chloroacetic acid is a commercially important halogenated acetic acid used primarily to make cellulose ethers and herbicides. It is also used in the manufacture of a variety of other chemicals listed in Subsection 3.4.2.

In 1983, 40 million pounds of chloroacetic acid were manufactured (18). At that time, the projected demand for 1987 was 68 million pounds (18). Currently it is being produced in the United States at two sites with estimated capacities of 25 and 30 million pounds each (37).

The major use of chloroacetic acid in the United States is for the manufacture of cellulose ethers (e.g., carboxymethyl cellulose), which in 1986, accounted for approximately 45 percent of the U.S. consumption (37). Chloroacetic acid is used to manufacture a variety of chemicals, including herbicides (40 percent); and thioglycolic acid and glycine (15 percent) (37).

3.4.1 Chemical Characteristics

Physical Properties and Hazards--

At room temperature, chloroacetic acid is a colorless, hygroscopic, crystalline solid. The physical properties of chloroacetic acid are listed in Table 3-11. Chloroacetic acid exists in four crystalline forms, with the alpha structure being the most stable and industrially important. It is soluble in water, methanol, acetone, diethyl ether, and ethanol.

Chemical Properties and Hazards--

The chemical properties of chloroacetic acid that contribute to the potential for an accidental release of the chemical include:

- Flammability - Chloroacetic acid is flammable at high temperatures and can form explosive mixtures in air at concentrations greater than 8 percent by volume chloroacetic acid.

TABLE 3-11. PHYSICAL PROPERTIES OF CHLOROACETIC ACID

		Reference
CAS Registry Number	79-11-8	
Chemical Formula	$C_2H_3ClO_2$	
Molecular Weight	94.50	
Normal Boiling Point	356 °F @ 14.7 psia	33
Melting Point	145.4 °F	33
Solid Specific Gravity (H_2O=1)	1.4043 @ 104 °F	39
Vapor Specific Gravity (air=1)	3.26	24
Vapor Pressure	0.065 mm Hg @ 77 °F	33
Vapor Pressure Equation[a]:		22

$$\text{Log } P_v = A - \frac{B}{T+C}$$

Where: Pv = vapor pressure, mm Hg
T = temperature, °C
A = 7.55016, a constant
B = 1,723.365, a constant
C = 179.98, a constant

		Reference
Liquid Viscosity	2.16 centipoise @ 158 °F	39
Solubility in Water	421 lb/100 lb H_2O @ 68 °F	39
Specific Heat at Constant Pressure	0.364 Btu/lb-°F @ 68 °F	39
Latent Heat of Vaporization	228 Btu/lb	39
Latent Heat of Fusion	88 Btu/lb	39
Liquid Surface Tension	35.17 dynes/cm @ 212 °F	39
Heat of Combustion	308,000 Btu/lb mole	39
Ignition Temperature	878 °F	39

(Continued)

TABLE 3-11 (Continued)

		Reference
Explosive Range, Volume % in air @ 1 atm	8 minimum; no maximum found reported	39
Flashpoint	258.8 °F	39

[a] This equation yields a vapor pressure of 11.2 psia rather than 14.7 psia at the boiling point. No explanation of this discrepancy was provided in the reference for vapor pressure but may be due to curve fit averaging of experimental data.

- Corrosivity - Chloroacetic acid is highly corrosive to most common metals.

- Decomposition - When heated to decomposition, chloroacetic acid may release highly toxic phosgene and hydrogen chloride vapor (38).

Toxicological and Health Effects--

Chloroacetic acid is highly toxic by ingestion and skin absorption. It is irritating to the skin, eyes, and respiratory tract, resulting in persistent burns. Ingestion can interfere with body enzyme systems and cause digestive tract perforation and peritonitis. More acute exposure can result in central nervous system and respiratory system depression. The probable lethal oral dose is between one teaspoon and one ounce for a 150-pound person (24). Death may also occur if more than 3 percent of the skin is exposed. The only exposure limit which has been set is an eight-hour time-weighted average of 0.13 ppm (20). The LC_{50} is 180 mg/m^3 for rats by inhalation (25).

3.4.2 Facility Descriptions

Chloroacetic Acid Manufacture--

Most chloroacetic acid is produced in the United States by the chlorination of acetic acid. Figure 3-6 illustrates a typical manufacturing process.

The process consists of sparging dry chlorine gas into liquid glacial acetic acid in a reactor. The reaction is carried out in the presence of catalytic quantities of sulfur or red phosphorous at temperatures between 185 and 250 °F (18,33). As the chloroacetic acid is formed, hydrogen chloride gas is evolved and recovered as hydrochloric acid by water scrubbing. The reactor contents are cooled to form chloroacetic acid crystals. A solvent is added, and dichloroacetic acid and unreacted acetic acid are extracted from the reaction mixture. An alternative purification process involves selective dechlorination of the dichloroacetic acid in the presence of hydrogen and a palladium catalyst at temperatures between 250 and 300 °F to form chloroacetic

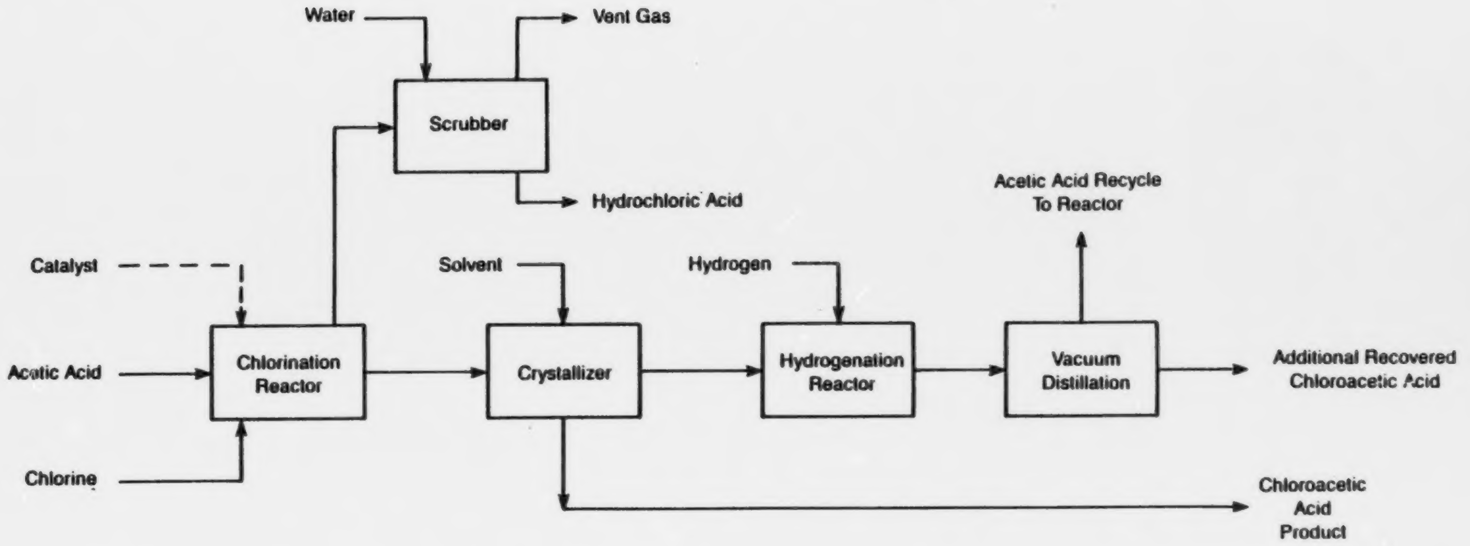


Figure 3-6. Conceptual flow diagram of typical chloroacetic acid manufacturing process

Adapted from: Reference 39

acid and acetic acid (39). The resulting stream is then separated by vacuum distillation to produce a product that is more than 99 percent chloroacetic acid (33,39).

Because of the highly corrosive nature of chloroacetic acid, the chlorination reaction is carried out in ceramic-lined, lead-coated steel, or glass-lined vessels (33,39).

Chloroacetic Acid Consumption--

The primary uses of chloroacetic acid in the United States are for the manufacture of cellulose ethers and herbicides. Additional uses of chloroacetic acid are for the manufacture of thiogycolic acid, glycine, ethyl acetate, and synthetic caffeine.

Cellulose Ethers--The largest end use of chloroacetic acid is for the manufacture of carboxymethyl cellulose. Figure 3-7 is a flow diagram of a typical manufacturing process.

In a typical continuous process, powered cellulose is fed to a rotary drum reactor. Chloroacetic acid and sodium hydroxide are added to the reactor through spray nozzles. The three materials react to form carboxymethyl cellulose. The reaction is exothermic, and cooling is required to maintain the reaction temperature between 77 and 160 °F (29). The crude product mixture is neutralized by adding acid and purified by extracting with methanol or methanol-water mixtures. The purified product is then dried and packaged. The efficiency of the reaction is approximately 60 to 80 percent (39). The remainder is transformed into sodium glycolate by hydrolysis of the chloroacetic acid.

Herbicides--The other major use of chloroacetic acid is for the manufacture of dichlorophenoxy and trichlorophenoxy acetic acid herbicides (i.e., 2,4-D and 2,4,5-T). These herbicides are manufactured by reacting aqueous chloroacetic acid with 2,4-dichlorphenol or 2,4,5-trichlorophenol in aqueous sodium hydroxide to form a sodium salt. The reaction is carried out at

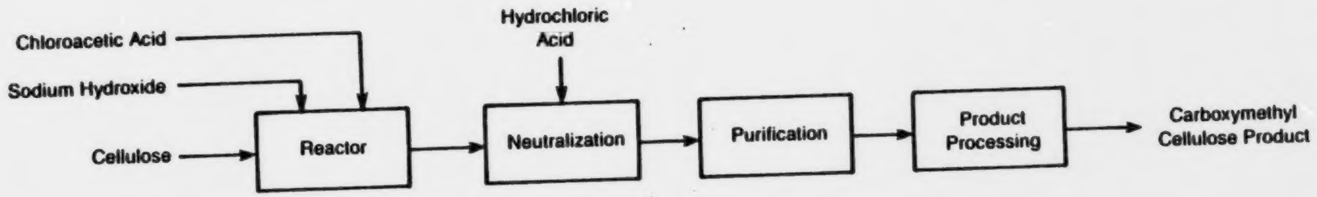


Figure 3-7. Conceptual flow diagram of carboxymethyl cellulose manufacturing process.

Adapted from: Reference 39

approximately 212 °F. The resultant salt is hydrolyzed to the free acid by adding hydrochloric acid. The corresponding acid is purified by recrystallization, filtered, and recovered as a final product.

3.4.3 Summary of Major Process Hazards and Control Technologies

For all processes, the accidental release risk can be reduced by applying specific measures broadly classified as prevention, protection or mitigation measures. These measures are discussed generically in Section 2 of this manual and are discussed in other technical literature.

The most significant property of chloroacetic acid that contributes to the risk of a release is its corrosivity.

Proper materials of construction must be used throughout the manufacturing, use, and storage systems. Particular attention should be paid to material selection for smaller equipment items such as pipe fittings because such items are frequently replaced, and proper material selection may be overlooked when repairs are made.

Below is a summary of hazard areas associated with chloroacetic acid manufacture, use and storage processes.

Cellulose Ethers Production--

Since the reaction during cellulose production is exothermic, a loss of cooling or reactant flow control could result in overheating and overpressure in the reactor; this, in turn, could lead to an accidental release of chloroacetic acid.

Herbicides--

In this production process, the chloroacetic and storage and feed systems are the locations with the greatest potential for an accidental release of chloroacetic acid. Probably the risk of a chloroacetic acid release from the reactor is low; however, a loss of flow control to the reactor could result in a release.

Table 3-12 presents examples of possible locations, conditions, and process hazards which could potentially lead to a chloroacetic acid release, as well as example controls for reducing the risk of such an event. The examples are intended to be illustrative, not exhaustive.

3.4.4 Storage and Handling

Table 3-13 lists materials of construction suitable and unsuitable for chloroacetic acid. Chloroacetic acid, which is highly corrosive to the metals commonly used as materials of construction for storage and process vessels, is stored as crystallized flakes, in molten form, or as an 80 percent aqueous solution. In molten form, it is transported in glass-lined tank cars and titanium-lined tank trucks and is stored in glass-lined containers (39). Aqueous solutions are handled in special stainless steel or rubber-lined containers below 100 °F and in iron containers with a baked phenolic resin coating below 212 °F (39). Flaked crystals are stored in polyethylene-lined fiber packs contained in fiberboard or iron drums. In addition, pipelines are commonly constructed of glass-lined steel or steel lined with polytetrafluoroethylene or perfluoroalkoxy polymers.

All Storage and Piping Systems--

Since most chloroacetic acid storage vessels and piping systems are constructed of lined materials, there is the potential for lining failure and a subsequent release because of corrosion. Linings should be routinely inspected. Some linings are particularly sensitive to failure by thermal cycling and shock, especially glass. While not generally a problem with plastics, it should not be completely disregarded. Linings are also subject to damage by mechanical shock. A perforation or crack in a lining will expose the underlying metal to attack by the chloroacetic acid. A small leak can lead to protracted corrosion ultimately leading to equipment failure and a release.

TABLE 3-12. EXAMPLE CONDITIONS, PROCESS HAZARDS AND HAZARD CONTROLS IN CHLOROACETIC ACID MANUFACTURING AND USE

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Carboxymethyl cellulose reactor or chlorination reactor	Excessively high chloroacetic acid feed rate; failure of cooling system	Excessive exothermic reaction causing overheating or overpressurization with equipment failure and release	High temperature alarm interlocked to flow control Limit maximum feed rates by flow limiting orifices or line sizes Backup cooling
	Excessive chloroacetic acid feed	Overfilling or overpressurization leading to release	Redundant level sensing with alarm and interlock to feed Overflow catch tank Strict high quality operating procedures and operator training
Process equipment handling chloroacetic acid	Formation of solid chloroacetic acid	Equipment plugging leading to overpressurization, overfilling, or backflow leading to release	Flow sensors with alarms Protection for pumps to prevent overpressure or overheating when flow is stopped Heat traced lines to prevent or melt plugs

(Continued)

TABLE 3-12. (Continued)

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Process equipment	Undetected corrosion	Equipment failure leading to release	Frequent equipment inspections Use of proper materials of construction Validation of materials of construction before equipment is installed
Process and storage vessels	Sparks or flame near vessels	Fire or explosion from overheating chloroacetic acid vessel or from ignition of leakage from vessel; fire or explosion could cause larger release	Improve fire protection Isolate chloroacetic acid storage from large concentrations of flammable materials and sources of ignition Pressure relief sized for fire

TABLE 3-13. ACCEPTABILITY OF VARIOUS METALS AND ALLOYS FOR CHLOROACETIC SERVICE

Material	Acceptable	Unacceptable
Aluminum		X
Brass		X
Carbon Steel		X
Copper		X
Hastelloy-B®	X	
Hastelloy-C®	X	
Inconel®		X
Lead		X
Monel®	X	
Nickel		X
Silver		X
Stainless Steel 316[a]	X	
Tantalum	X	
Titanium	X	
Zirconium	X	

Source: Adapted from Reference 40

[a] Reported in Reference 40. May only apply in special circumstances. Decomposition or reaction of chloroacetic acid to produce chlorides would appear to preclude use for some applications due to chloride stress corrosion cracking.

3.5 FURAN

Furan is a chemical intermediate used to manufacture pharmaceuticals, pesticides, herbicides, and fine chemicals. It is made commercially by decarbonylation of furfural and appears to be manufactured at a single site in the United States. Its use as a pesticide intermediate accounts for approximately 95 percent of the U.S. consumption.

3.5.1 Chemical Characteristics

Physical Properties and Hazards--

Furan is a clear, colorless, flammable liquid. The liquid turns brown on standing and has a strong odor similar to ether. It boils at 88.4 °F and one atmosphere of pressure to form a colorless, flammable, toxic gas. Table 3-14 lists the physical properties of furan. The combination of flammability and toxicity is especially hazardous since ignition of a leak could cause a fire or explosion that could result in a larger release.

Furan is only slightly soluble in water. It is miscible, however, in most common organic solvents. Furan vapor is 2.4 times more dense than air and will tend to stay close to the ground when released into the atmosphere. Liquid furan will expand slightly with heating. As a result, liquid-full equipment can pose a hazard.

Chemical Properties and Hazards--

The most significant chemical properties that may contribute to the potential for an accidental release of furan are:

- Furan is dangerous when exposed to heat or flame. Liquid furan has a low flash point, -32 °F, and high flammability. It is flammable in air at concentrations from 2.3 to 14.3 percent furan by volume.

TABLE 3-14. PHYSICAL PROPERTIES OF FURAN

		Reference
CAS Registry Number	110-00-9	
Chemical Formula	C_4H_4O	
Molecular Weight	68.08	
Normal Boiling Point	88.4 °F @ 14.7 psia	33
Melting Point	-122.08 °F	33
Liquid Specific Gravity (H_2O=1)	0.9371 @ 67 °F	21
Vapor Specific Gravity (air=1)	2.36	33
Vapor Pressure	9.54 psia @ 68 °F	21
Vapor Pressure Equation:		21

$$\text{Log} \quad Pv = A - \frac{B}{T+C}$$

Where: Pv = vapor pressure, mm Hg
T = temperature, ^{o}C
A = 6.97527, a constant
B = 1,060.87, a constant
C = 227.74, a constant

Liquid Viscosity	0.38 centipoise	21
Solubility in Water	1.0 lb/100 lb H_2O @ 77 °F	33
Specific Heat at Constant Pressure	0.406 Btu/(lb-°F) @ 77 °F	33
Latent Heat of Vaporization	171.2 Btu/lb	33
Liquid Surface Tension	24.10 dyne/cm @ 68 °F	21
Heat of Combustion	900,000 Btu/lb mole	33

(Continued)

TABLE 3-14. (Continued)

		Reference
Explosive Range, Volume % in air	2.3 min 14.3 max	33
Flashpoint, TCC (ASTM D-56)	-31.9 °F	33
Properties useful in determining other properties from physical property correlations.		
Critical Temperature	417.2 °F	33
Critical Pressure	772 psia	33

- Furan decomposes at 1,200 °F in the absence of catalyst and at 680 °F in the presence of nickel, to form a mixture consisting of carbon monoxide, hydrogen, and hydrocarbons (33).

- On exposure to air, furan can form unstable peroxides. Decomposition of these peroxides in furan equipment where unintentional exposure to air has lead to their formation could cause equipment failure and cause an accidental furan release.

- Furan is incompatible with strong acids and oxidizing agents. Contact with these materials can result in violent, exothermic reactions or corresponding overheating or overpressuring of equipment with containment failure and furan release.

Toxicological and Health Effects--

Little information is available on the toxological effects of accidental exposure to furan. Furan vapors are a central nervous system depressant. Exposure to furan can cause irritation and burning of the eyes and skin, dizziness, and suffocation. Furan is highly toxic by ingestion, inhalation, and skin absorption. No exposure limits have been determined for furan, although human exposures are routinely controlled to less than 10 ppm (33). The LD_{50} for mice via inhalation is 3500 ppm over 1 hour (41).

3.5.2 Facility Descriptions

Furan Manufacture--

Furan is manufactured commercially by the decarbonylation of furfural. Several furan manufacture reaction schemes have been patented (42). In all cases, the starting material for the manufacture of furan is furfural. The reaction can be carried out under catalytic or noncatalytic conditions, in the liquid or vapor phase. Figure 3-8 is a flow diagram of a typical manufacturing process.

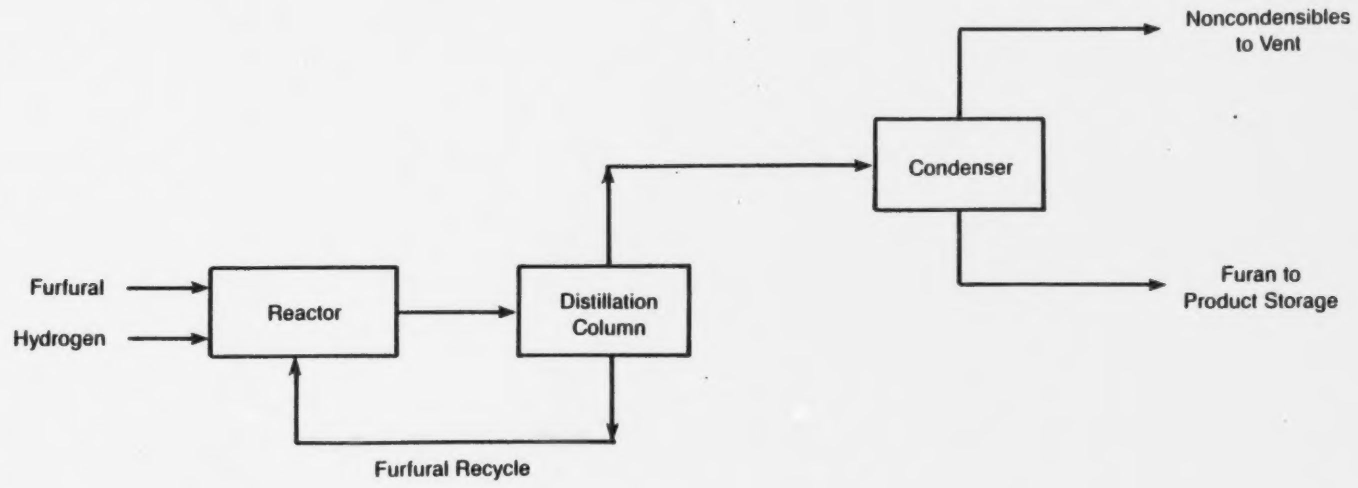


Figure 3-8. Conceptual flow diagram of typical furan manufacturing process.

Adapted from: Reference 42

A typical noncatalytic process is the pyrolysis of furfural at approximately 1,300 °F (33). The major drawback of noncatalytic processes is that they generate low yields of furan.

A typical catalytic process consists of passing furfural and hydrogen over a nickel or cobalt catalyst at approximately 540 °F to yield furan and carbon monoxide (42).

Whichever reaction type is used, the reaction products are fed to a distillation column that refluxes unreacted furfural to the reactor while allowing furan vapor to pass on to a condenser for product recovery. Any noncondensibles formed during the reaction, including carbon monoxide, are vented from the condenser.

Furan Consumption--

Furan is used as a chemical building block in the manufacture of a variety of chemical products, including: pharmaceuticals, herbicides, pesticides, stabilizers, and fine chemicals.

One such chemical is tetrahydrofuran. Tetrahydrofuran can be manufactured by the catalytic hydrogenation of furan in either the liquid or vapor phase (42). Figure 3-9 illustrates a typical vapor phase process. In this process, furan is vaporized and combined with a stream of hydrogen gas. The resulting gaseous mixture is then passed through a packed bed reactor containing a nickel catalyst. The reactor operates at a temperature of approximately 185 °F and a pressure of 1-2 pounds per square inch gauge (32). The vapor stream from the reactor contains essentially pure tetrahydrofuran, which is routed to a condenser for recovery of liquid product.

Thiophene can be manufactured by passing hydrogen sulfide and furan over an alumina catalyst at approximately 750 °F (33), as shown in Figure 3-10, producing thiophene and water. The water and thiophene are separated and the crude product is continuously distilled to the required purity. Pyrrole can be manufactured by passing furan, steam, and excess ammonia over an alumina

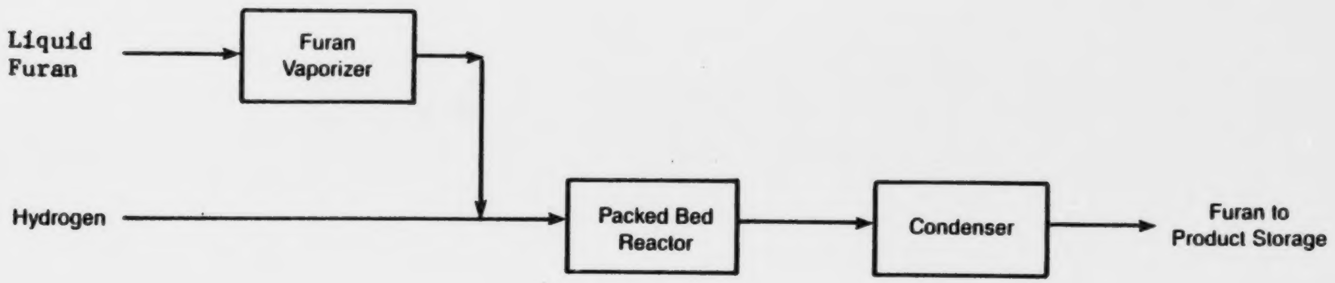


Figure 3-9. Conceptual flow diagram of typical tetrahydrofuran manufacturing process.

Adapted from: Reference 42

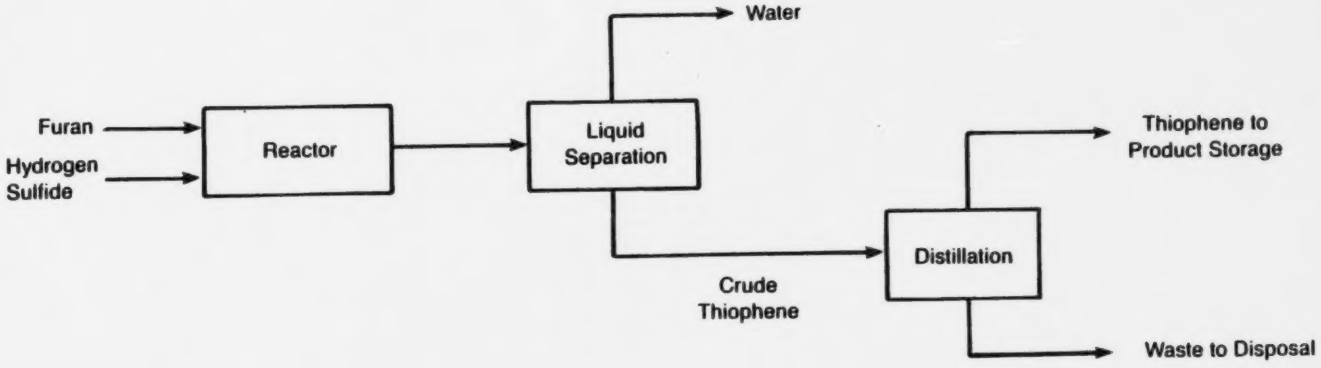


Figure 3-10. Conceptual flow diagram of typical thiophene manufacturing process.

Adapted from: Reference 33

catalyst at approximately 750-850 °F (29). The separation sequence is similar to that for thiophene.

Furan is also used in a variety of other organic syntheses, including the synthesis of polymeric compounds with ethylene for use as flocculants, pesticides, and pharmaceuticals.

3.5.3 Summary of Major Process Hazards and Control Technologies

To reduce the risk of an accidental release specific measures broadly classified as prevention, protection or mitigation measures may be applied. These measures are discussed generically in Section 2 and in greater detail elsewhere in the technical literature.

The properties of furan that contribute to the risk of a release are its low boiling point and flammability.

Below is a summary of hazard areas in the furan manufacturing, use and storage processes.

Furan Production--

Within this process, an accidental release of furan could result from a variety of sources. Three are mentioned below:

- Furan could thermally decompose if the temperature in the packed bed reactor exceeds 680 °F. This decomposition would cause the formation of two or more moles of gas per mole of furan, which could lead to overpressurization and accidental release.

- Lack of sufficient cooling in the distillation column condenser could cause overpressurization and release from the distillation column.

- Catalyst poisoning could result in an accumulation of unreacted furfural, which could lead to overpressurization and an accidental release.

Another hazard associated with this process is the potential for explosion since hydrogen is involved in a high-temperature reaction. Hydrogen is extremely explosive, and leaks of hydrogen can travel near the ground for long distances. The presence of trace quantities of oxygen in the reactor could cause an explosion. A hydrogen explosion could damage equipment that contains furan and result in a furan release.

Tetrahydrofuran Production--

The hazards associated with this process are similar to those associated with the furan production process. However, the temperature of this reaction is lower and the potential for thermal decomposition of the furan is less severe.

Thiophene and Pyrrole Production--

For both processes, a loss of flow or temperature control could result in thermal decomposition of furan, which could lead to an accidental release. In addition, the presence of oxygen in either of these reactions could cause a fire or explosion.

Storage and Handling--

Furan must be stored in the strict absence of oxygen. A reliable, and preferably dedicated inert gas system should be used for all storage vessels.

Table 3-15 presents examples of possible locations, conditions and process hazards which could potentially lead to a furan release, and example controls for reducing the risk of such a release. The examples are intended to be illustrative, not exhaustive.

TABLE 3-15. EXAMPLE CONDITIONS, PROCESS HAZARDS AND HAZARD CONTROLS FOR ACCIDENTAL FURAN RELEASES

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Packed bed reactor	Temperature exceeds 680°F	Overpressurization of equipment and relief valve discharge or equipment failure	Redundant temperature sensors and alarms
Distillation column condenser	Loss of cooling	Overpressurization and relief valve discharge	Redundant temperature sensors and and alarms; backup cooling system Adequate pressure relief Interlock to shut off reboiler feed if condenser cooling fails
Catalyst	Catalyst poisoning	Overpressure and relieve valve discharge	
Reactor	Presence of trace quantities of oxygen	Release of hydrogen and explosion, damaging furan-containing equipment ing release	Oxygen monitoring of reactor streams; oxygen alarm
Distillation column	Loss of flow control	Formation of peroxide and subsequent explosion	Redundant flow and temperature sensors with alarms Periodic cleaning of vessels where peroxide formation is possible Stringent inert gas system with oxygen monitoring

(Continued)

TABLE 3-15. (Continued)

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Distillation column	Loss of flow control	Formation of peroxide and subsequent explosions	Redundant flow and temperature sensors with alarms
			Periodic cleaning of vessels where peroxide formation is possible
			Stringent inert gas system with oxygen monitoring
Storage and process vessels	Nearby fire or explosion	Damage to furan containing equipment	Inert gas system for storage or process vessels
			Storage or process vessels isolated from potential sources of ignition
			Flammable gas detectors located throughout process or storage areas
			Adequate fire protection
			Pressure relief sized for heating due to fire

3.5.4 Storage and Handling

Furan must be stored in the strict absence of oxygen. A reliable, and preferably dedicated inert gas system should be used for all storage vessels. Inventories of furan should be rotated regularly and should be kept to a minimum. Long-term storage should never be attempted. Tanks should be emptied and cleaned routinely to remove any peroxide crystals that may form. However, extreme care should be taken to ensure an inert atmosphere before refilling such vessels with furan.

3.6 HYDRAZINE

Hydrazine has traditionally been recognized as a high-energy fuel for rockets and jets. Today, however, it is used primarily as a raw material in the manufacture of blowing agents for foamed plastics and in the production of pesticides. Hydrazine and derivatives are also used in water treatment.

All manufacture of hydrazine in the United States is currently based on the ketazine process. In 1983, approximately 18 million pounds of hydrazine were produced at two sites, each of which has a capacity of 14 million tons (18). These production data are based on non-fuel production because the production of hydrazine for fuel is erratic. However, it has been estimated that one million pounds of hydrazine were used as fuel in 1983 (18). In 1983, the non-fuel uses of hydrazine were as follows: herbicides, 53 percent; blowing agents for plastics, 27 percent; water treatment, 13 percent; other uses, 7 percent (18).

3.6.1 Chemical Characteristics

Physical Properties--

Hydrazine is a colorless, oily, fuming liquid at ambient conditions with an odor similar to ammonia. Table 3-16 lists the physical properties of anhydrous hydrazine.

Hydrazine is a strong reducing agent, weakly alkaline, and is very hygroscopic. It contracts upon freezing, so there is little danger of equipment rupture from formation of the solid. Hydrazine is soluble in water and other polar solvents such as alcohols, amines, and ammonia. The vapor is slightly more dense than air and will tend to stay close to the ground when released into the atmosphere.

Because liquid hydrazine will expand slightly when heated, liquid-full equipment can pose a hazard. A liquid-full vessel is an unvented vessel filled with liquid with little or no vapor space present above the liquid.

TABLE 3-16. PHYSICAL PROPERTIES OF HYDRAZINE

		Reference
CAS Registry Number	302-01-2	
Chemical Formula	N_2H_4	
Molecular Weight	32.05	
Normal Boiling Point	236.3 °F @ 14.7 psia	21
Melting Point	34.8 °F	21
Liquid Specific Gravity (H_2O=1)	1.008 @ 68 °F	43
Vapor Specific Gravity (air=1)	1.04 @ 68 °F	43
Vapor Pressure	0.28 psia @ 77 °F	33
Vapor Pressure Equation:		21

$$\log Pv = A - \frac{B}{T+C}$$

where: Pv = vapor pressure, mm Hg
T = temperature, °C
A = 7.8019, a constant
B = 1,679.07, a constant
C = 227.7, a constant

Liquid Viscosity	0.90 centipoise	33
Solubility in Water	Complete	33
Specific Heat at Constant Pressure	0.7358 Btu/(lb-°F) @ 68 °F	43
Latent Heat of Vaporization	602 Btu/lb @ 77 °F	43
Liquid Surface Tension	66.67 dynes/cm @ 77 °F	33
Heat of Combustion	270,000 Btu/lbmole	33
Autoignition Temperature	518 °F	43
Explosive Range, Volume % in air	4.7 min.	43

(Continued)

TABLE 3-16. (Continued)

		Reference
Flashpoint, COC	126 °F	43
Properties useful in determining other properties from physical property correlations.		
Critical Temperature	716 °F	43
Critical Pressure	2,130 psia	43
Critical Density	14.21 lb/ft^3	43

A liquid-full line is a section of pipe sealed off at both ends and full of liquid, with little or no vapor space. When there is no room for thermal expansion of the liquid, temperature increases can lead to containment failure.

Chemical Properties and Reactivity--

The most significant chemical properties contributing to the potential for an accidental release of hydrazine include:

- Flammability - Hydrazine is flammable in air at concentrations over 4.7 percent by volume and can decompose violently (see "Decomposition") (43).
- Reactivity - Hydrazine reacts exothermically with oxygen to form nitrogen and water. If a large liquid surface of hydrazine is exposed to air, spontaneous ignition can occur because of the heat evolved by oxidation with atmospheric oxygen. Hydrazine reacts with sodium or calcium hypochlorite to form nitrogen, water, and the corresponding salt. However, if both reactants are present in high enough concentrations, the reaction may occur violently.
- Decomposition - Thermal decomposition of hydrazine occurs at temperatures above approximately 320 °F (33). However, the decomposition temperature is significantly lowered in the presence of catalysts, including copper, cobalt, molybdenum, and iron oxides (rust) (33). At temperatures approaching the boiling point of hydrazine, certain metals such as copper and molybdenum act as catalysts, leading to the decomposition of hydrazine. This can result in overpressure of storage and process vessels.
- Instability - Liquid hydrazine is stable to shock. However, sudden violent movement can cause hydrazine vapor to detonate when it is within the flammable limits (43,44).

Toxicological and Health Effects--

Hydrazine is highly toxic by ingestion, inhalation, and skin absorption. Symptoms of exposure to hydrazine include eye, nose, and throat irritation, temporary blindness, dizziness, nausea, dermatitis, and skin and eye burns (38). Inhalation may cause nausea, headache, facial numbness, twitching, sore throat, and pulmonary edema (24). In addition, since prolonged exposure to hydrazine vapors causes a deadening of the sense of smell, detection of hydrazine by odor can be used only as an initial warning. According to the International Agency for Research on Cancer (IARC), there is sufficient animal evidence that hydrazine is a carcinogen (25). The Occupational Safety and Health Administration (OSHA) standard in air for hydrazine is a time-weighted average of 0.1 ppm over an 8-hour day. Hydrazine is especially hazardous by dermal exposure (25). Table 3-17 summarizes some of the relevant exposure data for hydrazine.

3.6.2 Facility Descriptions

Hydrazine Manufacture--

Hydrazine is manufactured by the partial oxidation of ammonia with chlorine, hypochlorite, or hydrogen peroxide. Current U.S. production is based on the ketazine process (18). Figure 3-11 is a flow diagram of a typical ketazine process. In this process, sodium hypochlorite, aqueous ammonia, and acetone are fed to a reactor that operates under slight pressure and at a temperature of 85-100 °F (33). The reactor product stream, containing 1-2 percent hydrazine, is sent to an ammonia recovery system where the unreacted ammonia is stripped, absorbed in water and returned to the reactor. The bottoms stream from the ammonia recovery system consisting of hydrazine, ketazine, water and sodium chloride salt, is fed along with additional acetone to a distillation column, where the sodium chloride is removed.

The remaining materials (water, hydrazine and ketazine) are taken overhead and fed to a pressure hydrolysis column. In the hydrolysis column, the ketazine reacts with water to form acetone and hydrazine. The column operates at approximately 10 atm (33). Acetone is taken overhead and is recycled to

TABLE 3-17. LC_{50} OR LD_{50} DATA FOR HYDRAZINE

Route of Exposure	Species	LC_{50} or LD_{50}	No. of Doses or Duration of Dosage
oral	Rat	60 mg/kg	Once
inhalation	Rate	570 ppm	4 hr
inhalation	Mouse	252 ppm	4 hr
intraperitoneal	Rat	59 mg/kg	Once
intravenous	Rabbit	26 mg/kg	Once
dermal	Rabbit	93 mg/kg	Once
dermal	Guinea pig	190 mg/kg	Once

Source: Reference 25

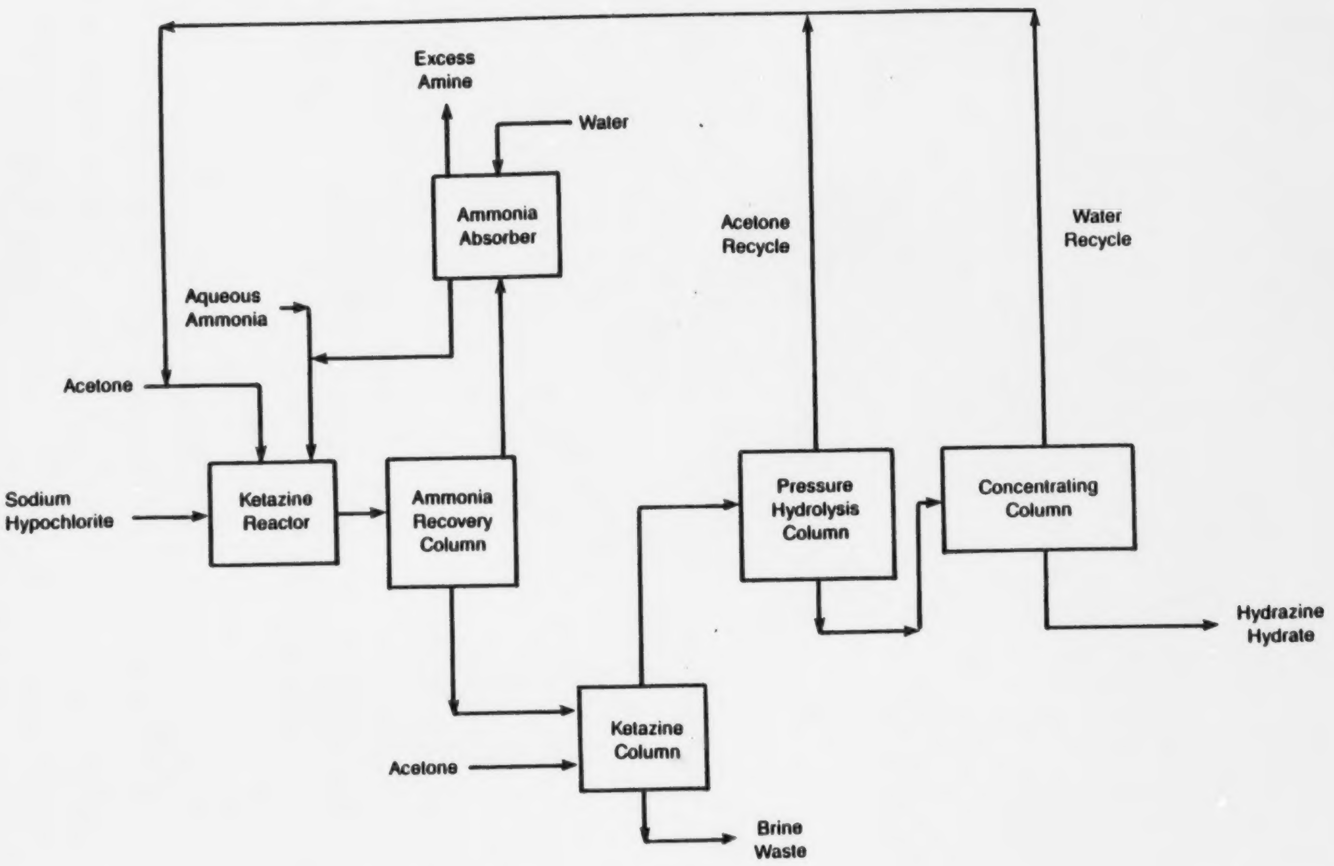


Figure 3-11. Conceptual flow diagram of typical ketazine-based hydrazine hydrate manufacturing process.

Adapted from: Reference 33

the ketazine reactor. The bottom stream, consisting of a 10 to 12 percent hydrazine solution, is sent to a concentrating column where water is taken overhead and recycled to the ketazine reactor while hydrazine hydrate is withdrawn from the bottom as product. The concentration of the hydrazine hydrate can be varied to produce the several aqueous grades available commercially: 64, 54.4, and 35 percent hydrazine (33).

In addition to hydrazine hydrate, anhydrous hydrazine is also produced. As shown in Figure 3-12, the hydrate and aniline are fed to an azeotrope column. The bottoms from the azeotrope column, consisting of aniline and hydrazine, are sent to a final hydrazine column where anhydrous hydrazine is taken as an overhead product.

Hydrazine Consumption--

The primary uses of hydrazine in the United States are for manufacturing agricultural chemicals and chemical blowing agents for foamed plastics, as a high energy fuel (e.g., rocket fuel), and for boiler water treatment. Table 3-18 lists some additional end uses of hydrazine. Most commercial applications use hydrazine hydrate in various concentrations. One exception is for high energy fuel consumption, in which anhydrous hydrazine is used.

Agricultural Chemicals--

Hundreds of hydrazine derivatives have been patented for use in agriculture. Table 3-19 lists some of the most common. The reader can refer to the patent literature for specific process information on a specific chemical.

Blowing Agents--

Chemical blowing agents refer to substances that create a foaming action in polymers to form foamed plastics. The blowing agent decomposes during extrusion to form the foam. Several hydrazine-based blowing agents are currently used. The blowing agent produced in the largest volume is azodicarbonamide.

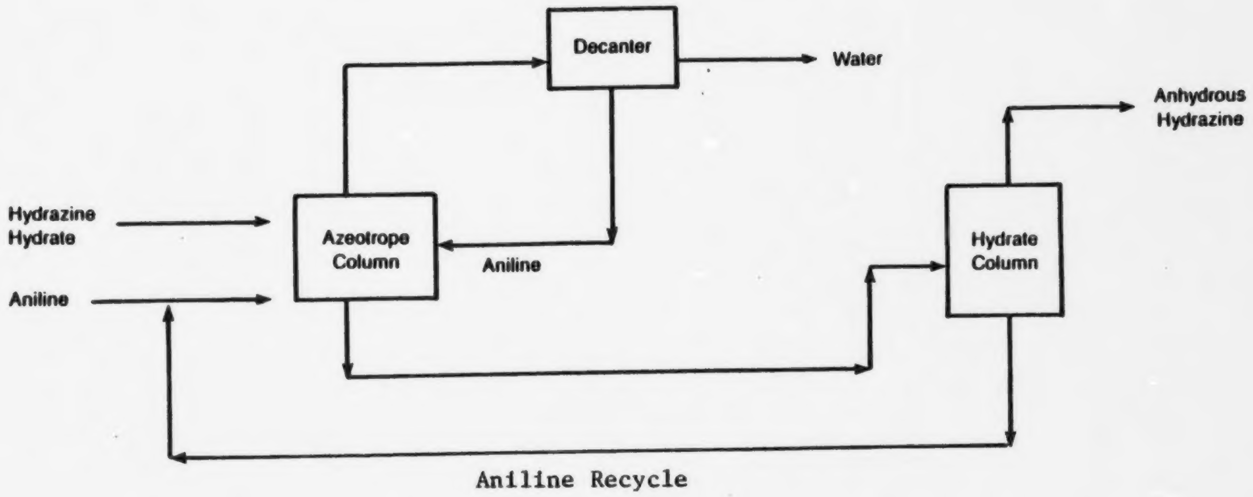


Figure 3-12. Conceptual flow diagram of typical anhydrous hydrazine separation process.

Adapted from: Reference 33

TABLE 3-18. TYPICAL END USES OF HYDRAZINE

Agricultural Chemicals
Blowing Agents for Foamed Plastics
Food-Grade Hydrochloric Acid Manufacture
Fuel for Fuel Cells
Oxygen Scavenger for Boiler Water
Rocket Fuel
Spandex® Fibers
Soldering Fluxes
Tetracene

Source: Reference 17

TABLE 3-19. COMMON HYDRAZINE-BASED BIOCIDES AND GROWTH REGULATORS

Common Name	Use
Aminocide	Plant growth regulator
Amitrole	Herbicide
Azinphosethyl	Insecticide
Benquinox	Fungicide
Credazine	Herbicide
Difenzoquat	Herbicide
Drazoxolon	Fungicide
Maleic hydrazide	Plant growth regulator
Methidathion	Insecticide
Metribuzin	Herbicide
Norflurazone	Herbicide
Oxadiazon	Herbicide
Pyrazon	Herbicide
Pyrazophos	Fungicide
Tebuthiuron	Herbicide

Source: Reference 28

Hydrazine and urea are the starting materials for azodicarbonamide. An intermediate, hydrazodicarboxamide, is prepared by refluxing an aqueous solution of urea and hydrazine. Azodicarbonamide is then formed by the oxidation of this intermediate. Additional information on hydrazine-based blowing agents can be obtained from the technical literature.

Water Treatment--

Hydrazine is used by public utilities, pulp and paper, textile and chemical processing plants for corrosion protection in boilers, hot-water heating systems and waste steams (33).

Hydrazine is useful for controlling corrosion because it reacts with oxygen to form nitrogen and water. Hydrazine also reacts with iron to form magnetite on metal surfaces, which provides a protective coating against additional corrosive attack. Generally, less than 0.1 ppm hydrazine is required for full corrosion protection of equipment (33).

Propellants--

The first use of anhydrous hydrazine was as a rocket fuel (33), because when hydrazine contacts certain oxidizers (e.g., nitrogen tetroxide), the mixture ignites with instantaneous total conversion of all reactants. Today, hydrazine is still used as a high-energy fuel, although its use has declined.

3.6.3 Summary of Major Process Hazards and Control Technologies

To reduce the risk of an accidental release, specific measures broadly classified as prevention, protection or mitigation measures may be applied. These measures are discussed generally in Section 2 in this manual and are discussed in more detail in other technical literature.

The properties of hydrazine that contribute to the risk of a release are its explosivity and flammability. Below is a summary of hazard areas in the hydrazine manufacturing, use and storage processes.

Hydrazine Manufacture--

Since the hydrazine in the ketazine process is almost always present in low concentrations, the potential for a hydrazine accidental release is low. The highest hydrazine release hazard area is probably the concentrating column. A loss of cooling to the condenser or a loss of temperature control in the reboiler could result in an overpressure and an accidental release.

Handling anhydrous hydrazine at elevated temperatures creates a potential for an accidental hydrazine release. A loss of temperature control in the final hydrate column could lead to hydrazine decomposition and an accidental release. The presence of oxygen could cause an explosion.

A small leak of hydrazine is likely to result in a fire, which could lead to a large hydrazine release. However, the released hydrazine would probably burn; therefore, the greatest danger is probably the destruction associated with a fire or explosion rather than the toxicological effects of exposure to hydrazine.

Agricultural Chemical Production--

For all the agricultural chemical production processes, the greatest hazard is the potential for a hydrazine-induced fire or explosion rather than acute hydrazine exposure. The use of hydrazine in an aqueous solution substantially reduces the risk. Fires or explosion are most likely to occur whenever hydrazine vapors are present and wherever oxygen is allowed to contact the hydrazine.

Blowing Agents Production--

The accidental release hazard for this process, which is similar to those for agricultural chemical manufacturing processes, is that if unreacted hydrazine comes in contact with the oxidizer in the second reaction, a potentially explosive reaction could result.

Water Treatment Facilities--

The hydrazine accidental release potential is very low in facilities that use the chemical for water treatment because the hydrazine inventories at these facilities are small. However, a small inventory should still be treated with caution since a small release could result in a fire that could lead to a larger process upset.

Table 3-20 presents examples of possible locations, conditions and process hazards which could potentially lead to a hydrazine release, and example controls for reducing the risk of such a release. The examples are intended to be illustrative, not exhaustive.

3.6.4 Storage and Handling

In the United States, hydrazine is stored in drums, bulk storage tanks, and railroad tank cars and tank trucks used for temporary stationary storage. Table 3-21 lists materials of construction compatible with hydrazine for storage and process vessels.

Large quantities of hydrazine are typically stored in pressure vessels. Each tank is typically electrically grounded and fitted with a level gauge, pressure gauge, relief valve, and flame arrester on its top (44,45). Nitrogen or another inert gas blanket is used to prevent the formation of flammable mixtures. Hydrazine must be stored away from sources of ignition and away from oxidants. Carbon dioxide should not be used as a blanketing gas since hydrazine reacts to form a carbazic acid salt (33). In addition, all transfer and storage systems must be free of air, since hydrazine reacts violently with oxygen.

Hydrazine is usually transferred by pressurizing the storage vessel with dry inert gas (e.g., nitrogen), or by using a transfer pump constructed of compatible materials.

Hydrazine fires can be controlled by deluging with water, which should generally be applied as a spray rather than a fog (43).

TABLE 3-20. EXAMPLE CONDITIONS, PROCESS HAZARDS AND HAZARD CONTROLS IN HYDRAZINE MANUFACTURING AND USE

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Distillation columns for anhydrous hydrazine production	Excess hydrazine feed; loss of condenser cooling	Overfilling leading to release; overpressurization causing equipment failure and release	High level alarms interlocked to flow control Overflow catch tank Adequate sizing of pressure relief to handle maximum flow Pressure relief discharge sent to flare Redundant temperature sensors with alarms Interlock to shut off reboiler heat if condenser cooling fails
Process or storage areas	Spark or flame near hydrazine facilities	Loss of containment	Hydrazine storage isolated from sources of flame High quality fire protection Explosion proof electrical equipment Flammable gas detectors around process and storage areas interlocked to a sprinkler system

(Continued)

TABLE 3-20. (Continued)

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Process or storage areas	Loss of inert gas blanket	Formation of explosive mixture	Flammable gas detectors inside storage vessels Backup inert gas system Flame arresters on any vent connections
Ketazine reactor in hydrazine manufacturing process	Loss of temperature control	Thermal decomposition and overpressurization leading to relief valve discharge or equipment failure and release; possible fire or explosion	Backup cooling system with redundant control Maximum feed rates limited by flow restrictions to reduce the potential for a runaway reaction Blast shields around high hazard equipment
Concentrating column in hydrazine manufacturing process	Loss of cooling in condenser or temperature control in reboiler	Overpressurization leading to relief valve discharge or equipment failure and release	Relief valve; redundant temperature sensors and alarms; high reliability controls; interlock to shut off reboiler heat if condenser cooling fails
Final hydrate column in anhydrous hydrazine manufacturing process	Loss of temperature control	Hydrazine decomposition leading to overpressurization and relief valve discharge or equipment failure and	High reliability heating controls; redundant temperature sensing and alarms; interlock to shut off heating with excess temperature or failure of condenser cooling

TABLE 3-21. MATERIALS OF CONSTRUCTION REPORTED TO BE COMPATIBLE WITH HYDRAZINE

Compatible with Hydrazine

Aluminum Alloy Nos. 356, B356, 1100, 2014, 2024, 4043, 5052 6061, 6066, and Tens 50
Chromium plating
Graphite
Inconel®
Inconel-X®
Kel-F®
Polyethylene
Stainless Steel 304, 321, 347, and 1707 pH
Teflon®

Not Compatible with Hydrazine

Carbon Steel
Copper

Hastelloys®
Magnesium
Iron
Nickel
Stainless Steel AM-350 and AM-355
Monel®
Lead
Zinc

Source: References 43 and 44

3.7 HYDROGEN SULFIDE

Hydrogen sulfide is a colorless gas used in the manufacture of numerous sulfur compounds, especially various inorganic sulfides, and alkyl mercaptans. A detailed discussion of uses appears in Subsection 3.7.2.

Little information is currently available concerning the size of the U.S. market for hydrogen sulfide; however, it appears to be currently manufactured at ten sites in the United States. It is used primarily in manufacturing sulfur, sulfuric acid, sulfur dioxide, sodium sulfide, and miscellaneous mercaptans (33).

3.7.1 Chemical Characteristics

Physical Properties and Hazards--

Hydrogen sulfide is a colorless, flammable, toxic gas at ambient conditions, with a characteristic odor of rotten eggs. Table 3-22 lists the physical properties of hydrogen sulfide. Hydrogen sulfide is only slightly soluble in water; however, it is soluble in some organic solvents and it is very soluble in alkanolamines, which are often used as scrubbing solvents to remove hydrogen sulfide from gas streams. Hydrogen sulfide is slightly more dense than air and will tend to stay close to the ground when released to the atmosphere at ambient temperatures.

Because liquid hydrogen sulfide has a large coefficient of thermal expansion, liquid-full equipment can pose a special hazard.

Chemical Properties and Hazards--

The chemical properties of hydrogen sulfide that contribute to the potential for an accidental release include:

- Flammability - Hydrogen sulfide is flammable in air at concentrations from 4.3 to 46 percent by volume of hydrogen sulfide.

TABLE 3-22. PHYSICAL PROPERTIES OF HYDROGEN SULFIDE

		Reference
CAS Registry Number	7783-06-4	
Chemical Formula	H_2S	
Molecular Weight	34.08	
Normal Boiling Point	-76.6 °F @ 14.7 psia	46
Melting Point	-117.2 °F	46
Liquid Specific Gravity (H_2O=1)	0.916 @ -76.6 °F	33
Vapor Specific Gravity (air=1)	1.19	33
Vapor Pressure	149.9 psia @ 68 °F	33

Vapor Pressure Equation:

$$\log Pv = A - \frac{B}{T+C}$$

where: Pv = vapor pressure, mm Hg
T = temperature, °C
A = 6.99392, a constant
B = 768.130, a constant
C = 249.09, a constant

Liquid Viscosity	0.412 centipoise @ 32 °F	21
Solubility in Water	0.398 lb/100 lb H_2O @ 68 °F	33
Specific Heat at Constant Pressure	0.2532 Btu/(lb-°F) @ 70 °F	46
Latent Heat of Vaporization	236.3 Btu/lb	46
Liquid Surface Tension	59.6 dyne/cm @ -76.6 °F	21
Heat of Combustion	8,340 Btu/lb	46
Autoignition Temperature	500 °F	33
Explosive Range, Volume % in air @ 1 atm @ 68 °F	4.3 min. 46 max.	33

(Continued)

TABLE 3-22 (Continued)

		Reference
Additional properties useful in determining other properties from physical property correlations.		
Critical Temperature	212.7 °F	46
Critical Pressure	89 atm	46
Critical Density	21.8 lb/ft^3	46

- Corrosivity - Dry, pure hydrogen sulfide does not react with common metals at ordinary temperatures. However, in the presence of air or moisture, hydrogen sulfide is very corrosive to metals.

- Reactivity - Hydrogen sulfide reacts rapidly with strong oxidizing agents.

Toxicological and Health Effects--

Hydrogen sulfide is a highly toxic and asphyxiant gas that acts directly on the central nervous system to cause paralysis of the respiratory system. Hydrogen sulfide has a sweet odor at concentrations between 30 and 100 ppm and deadens the sense of smell above this range (46). Relying on its rotten egg odor can prove dangerous in certain situations.

The effects of hydrogen sulfide exposure vary, depending on the level of exposure. Low level exposure may cause headache, nausea, fatigue, inflammation of the eyes and mucous membranes, labored breathing, digestive tract disorders, vomiting, and diarrhea. More severe exposure can cause rapid heart rate, weakness, sudden collapse, unconsciousness, and death. Acute exposure can cause immediate death. Table 3-23 summarizes some of the relevant exposure limits of hydrogen sulfide. Table 3-24 summarizes the human health effects of exposure to various concentrations of hydrogen sulfide.

3.7.2 Facility Descriptions

This subsection provides brief descriptions of the manufacture and uses of hydrogen sulfide in the United States. Major accidental release hazards of these processes are discussed in Section 3.7.4.

Hydrogen Sulfide Manufacture--

Most hydrogen sulfide produced in the United States is either a byproduct of other processes or is obtained from natural gas contaminated with hydrogen sulfide (33). Most hydrogen sulfide is sold as a liquified gas.

TABLE 3-23. EXPOSURE LIMITS FOR HYDROGEN SULFIDE

Limit	Concentration (ppm)	Description	Reference
IDLH	300	The concentration defined as posing an immediate danger to life and health (i.e. causes irreversible toxic effects for a 30-minute exposure).	23
PEL	20	A time-weighted 8-hour exposure to this concentration, as set by the Occupational Safety and Health Administration (OSHA), should result in no adverse effects for the average worker.	23
LC_{LO}	600	This concentration is the lowest published lethal concentration for a human over a 30-minute exposure.	25

TABLE 3-24. EFFECTS OF HYDROGEN SULFIDE INHALATION

Concentration (PPM)	Effect of Exposure
20-150	Severe burning of eyes, headache, dizziness, conjunctivitis
500	For 30 minutes, headache, dizziness, excitement, staggering, bronchitis, bronchial pneumonia.
<600	For 30 minutes, fatal through respiratory paralysis.

Source: Reference 46

The natural gas industry produces the largest quantity of by-product hydrogen sulfide. The natural gas processing units use an amine solution to absorb the hydrogen sulfide to "sweeten" the natural gas. Figure 3-13 illustrates this type of process. The recovered hydrogen sulfide is usually used either as a feedstock for commercial sulfur recovery or sulfuric acid production, or is flared or incinerated.

In petroleum refining, 90 percent of the sulfur accumulates in the gas oil and coke-distillate fractions. Sulfur is removed by passing the sulfur-rich fractions through a fixed bed catalyst with hydrogen, which converts 80-90 percent of the sulfur to hydrogen sulfide and increases hydrocarbon saturation. Concentrated in this manner, the sulfur is then recovered by converting the hydrogen sulfide to sulfur in a Claus unit or equivalent process.

Several commercial processes have been developed for the manufacture of hydrogen sulfide from heavy fuel oils and sulfur and from methane, water vapor, and sulfur. One such process is carried out in two steps. The first step reacts methane with sulfur to form carbon disulfide and hydrogen sulfide. This is followed by the hydrolysis of carbon disulfide to hydrogen sulfide.

Hydrogen sulfide is also manufactured by directly combining hydrogen gas with elemental sulfur. In this process, hydrogen and sulfur vapor react at approximately 950 °F in the presence of an alumina catalyst (33). This reaction can also be carried out at elevated temperature and pressure without a catalyst (46).

Hydrogen Sulfide Consumption--

Hydrogen sulfide is captured primarily in acid gas recovery and sulfur recovery processes. The acid gas recovery usually acts as a feed to the sulfur recovery process. Most hydrogen sulfide recovered as a by-product is converted to elemental sulfur. Hydrogen sulfide is also used to manufacture sulfuric acid and inorganic sulfides, including sodium sulfide and sodium hydrosulfide, and a variety of mercaptans. Table 3-25 lists some end uses of hydrogen sulfide.

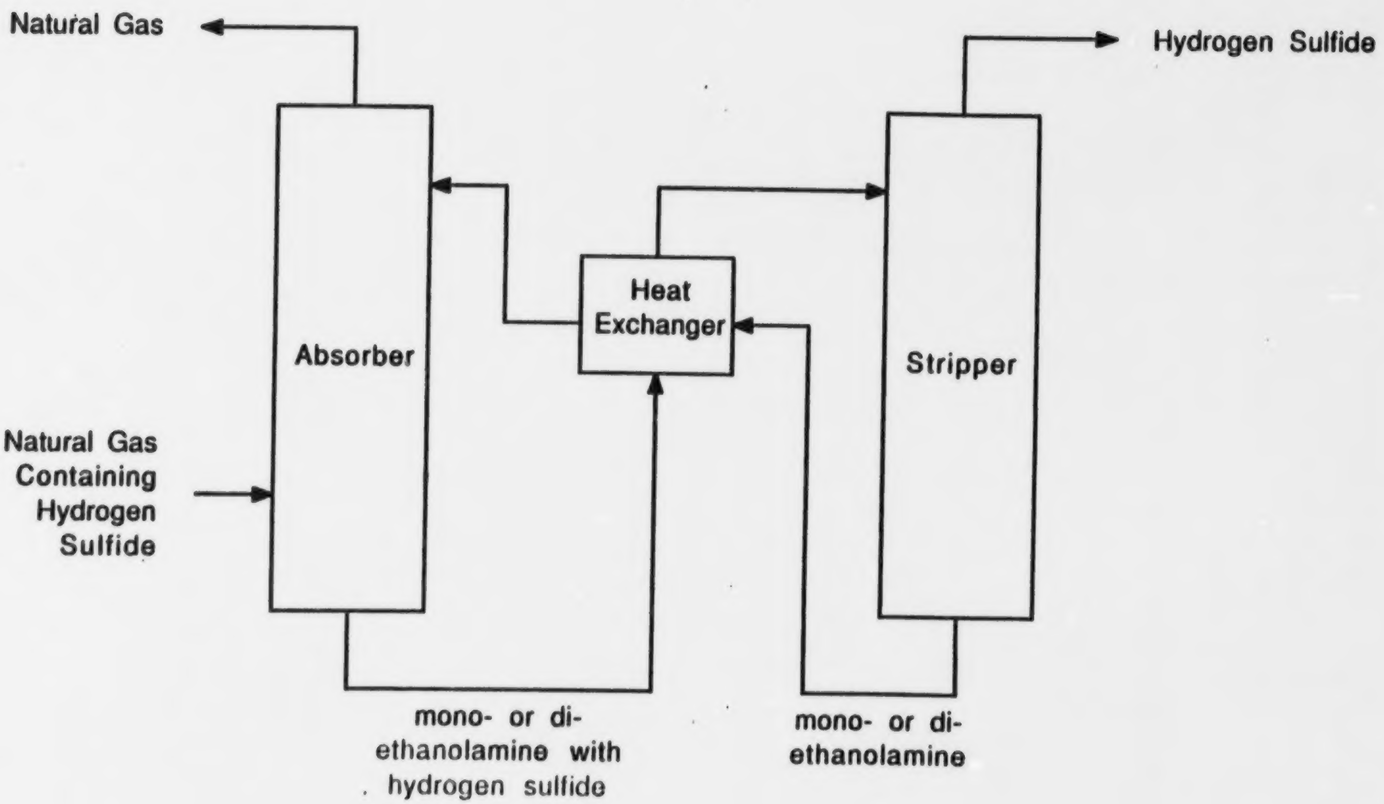

Natural Gas
Hydrogen Sulfide
Absorber
Heat Exchanger
Stripper
Natural Gas Containing Hydrogen Sulfide
mono- or di-ethanolamine with hydrogen sulfide
mono- or di-ethanolamine

Figure 3-13. Conceptual flow diagram of a process for absorbing hydrogen sulfide.

Adapted from: Reference 33

TABLE 3-25. TYPICAL END USES OF HYDROGEN SULFIDE

- Alkyl Mercaptans:
  - Butyl Mercaptan
  - Dodecyl Mercaptan
  - Ethyl Mercaptan
  - Methyl Mercaptan
  - Propyl Mercaptan
- Ammonium Polysulfide
- Ammonium Sulfide
- Dimethyl Sulfide
- Mercaptobenzothiazole
- Mercaptoethanol
- Mercuric Sulfide
- Molybdenum Disulfide
- Potassium Hydrosulfide
- Sodium Hydrosulfide
- Sodium Sulfide
- Sulfur
- Sulfur Dioxide
- Sulfuric Acid

Source: Reference 47

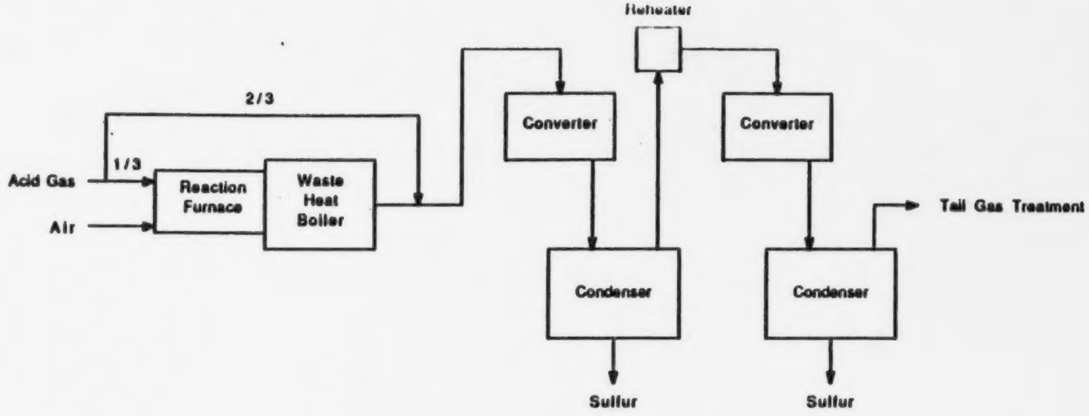
Sulfur Production--

The Claus process is the most widely used process for converting hydrogen sulfide into elemental sulfur. The Stretford process, a combination process that sweetens the feed gas and produces elemental sulfur, is also prominent. Figure 3-14 shows two configurations of the Claus process.

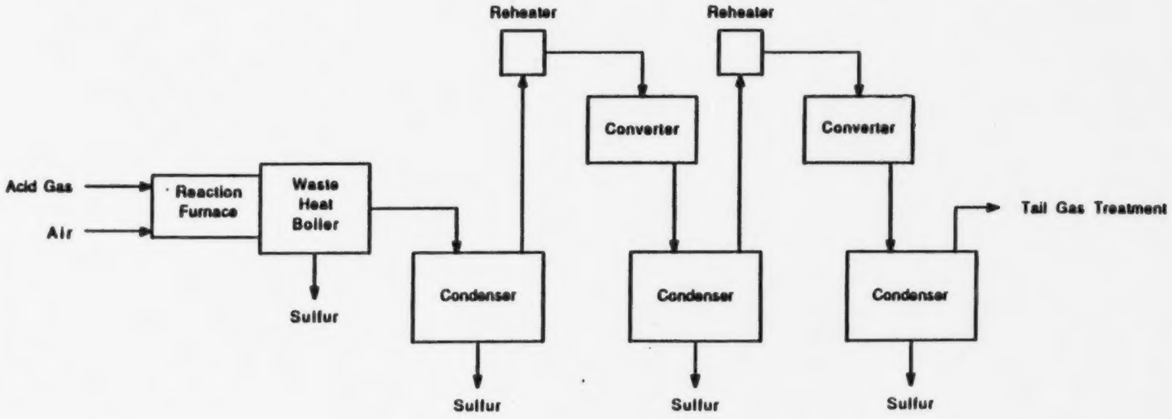
The process consists of a combustion stage catalytic converter and a tail gas cleanup stage. After entering the combustion stage, a portion of the hydrogen sulfide is converted to sulfur dioxide. The sulfur dioxide and remaining hydrogen sulfide react (usually in a catalytic converter) to produce elemental sulfur, which is removed as a liquid in the condenser. The process stream enters a reheater, passes to another converter, and condenses again. The reheater-converter-condenser stages are linked in series to enhance removal of hydrogen sulfide. Because most Claus plants are unable to meet new air pollution regulations for sulfur dioxide, the tail gas often goes to an additional treatment process where residual hydrogen sulfide is removed (33).

In the Stretford process, hydrogen sulfide is absorbed into an alkaline solution. The absorber solution is sent to a reactor where the hydrogen sulfide is oxidized by vanadium to produce elemental sulfur. The alkaline mixture of sulfur and reduced vanadium is sent to a series of vessels where the sulfur is removed and the vanadium is oxidized and recycled (49).

When hydrogen sulfide is converted to sulfur, usually the hydrogen sulfide is present in the initial gas stream in a dilute form. If the initial hydrogen sulfide extraction column failed to extract the chemical, then the hydrogen sulfide would exit with the gas stream. The consequences of this would depend on the concentration of hydrogen sulfide in the gas stream and on the ultimate destination of the gas stream. In most cases, the hydrogen sulfide would probably be released to the atmosphere with the gas stream. The hydrogen sulfide absorption column could fail if it were contaminated with acid or if the scrubber liquid circulation pump were to fail, or if the scrubber was not kept at a low enough temperature.



Split - flow configuration



Straight - through configuration

Figure 3-14. Conceptual flow diagram of two configurations of the Claus process.

Adapted from: Reference 48

Sodium Sulfide Production--

Hydrogen sulfide is used for the manufacture of sodium sulfide. In this process, hydrogen sulfide is bubbled through an excess of sodium hydroxide in water, where sodium sulfide and water are formed. The reaction is exothermic and heat is removed either by evaporating water from the mixture or by cooling. The product mixture is often concentrated by evaporation to 60 weight percent sodium sulfide (33).

Sulfuric Acid Production--

Occasionally, hydrogen sulfide is used to produce sulfuric acid. In this process hydrogen sulfide is burned in air to produce sulfur dioxide. The sulfur dioxide is then catalytically converted to sulfur trioxide, which is hydrated to sulfuric acid by absorption into an aqueous sulfuric acid stream (33).

Mercaptan Production--

Most mercaptans are made by reacting hydrogen sulfide with olefins or alcohols (33). The details of the process will depend on the specific olefin or alcohol used. For example, ethyl mercaptan can be manufactured by exposing a continuous stream of ethylene and excess hydrogen sulfide vapors to ultraviolet light. The excess hydrogen sulfide can be stripped from the product ethyl mercaptan and recycled back to the reactor.

3.7.3 Summary of Major Process Hazards and Control Technologies

To reduce the risk of an accidental release, specific measures broadly classified as prevention, protection or mitigation measures may be applied. General features of these measures are discussed in Section 2 and are presented in greater detail in other technical literature.

The properties of hydrogen sulfide that contribute to the risk of a release are its corrosiveness and flammability. Hydrogen sulfide releases can originate from many sources, including ruptures in process equipment, separated flanges, actuated relief valves or rupture disks, leaks at joints and connections, and failed pumps.

Since hydrogen sulfide has a deceptively sweet smell at 30-100 ppm concentrations and deadens the sense of smell above these levels, hydrogen sulfide vapor detection devices should be located throughout facilities that store and handle hydrogen sulfide. Enclosures for hydrogen sulfide storage vessels or process facilities should be used with extreme caution because toxic concentrations can accumulate.

Below is a summary of hazard areas in the hydrogen sulfide manufacturing, use and storage processes.

Hydrogen Sulfide Production--

For all hydrogen production processes, the primary hydrogen sulfide release hazards are in the final hydrogen sulfide purification steps. In all cases, the reactors used to recover or produce hydrogen sulfide have low inventories of dilute hydrogen sulfide and therefore a low risk of accidentally releasing hydrogen sulfide.

Most of the processes incorporate a final distillation step where the purified hydrogen sulfide is removed, and a large in-process inventory of hydrogen sulfide is present during this step. A condenser coolant failure could lead to an overpressure followed by an accidental release. Corrosion or wear of pumps and piping systems could also result in a release.

Sodium Sulfide Production--

During sodium sulfide production, as long as there is an excess of sodium hydroxide, there is little chance of an accidental release of hydrogen sulfide. However, a loss of feed or composition control could result in incomplete reaction and hydrogen sulfide pressure could build in the reaction vessel and be accidentally released. In addition, a loss of temperature control in the reactor could raise the temperature to a point where the hydrogen sulfide escapes before reacting, which could lead to an accidental release as a result of hydrogen sulfide pressure in the reactor. Where mechanical agitation is required, a loss of agitation could also result in incomplete reaction and hydrogen sulfide overpressure.

Sulfuric Acid Production--

As long as sufficient air is available, there is little chance of a hydrogen sulfide release from this process. However, a loss of air supply could result in an accumulation of unreacted hydrogen sulfide, leading to an accidental release.

Mercaptan Production--

Because most mercaptans are manufactured with an excess of hydrogen sulfide, the potential exists for a hydrogen sulfide release from the hydrogen sulfide recirculation equipment. Pumps, valves, and piping in the recirculation system are all potential sources of a hydrogen sulfide release. Also, all mercaptan manufacturing processes involve a catalyst. Deactivation of the catalyst could result in an incomplete reaction, which would result in an accumulation of unreacted hydrogen sulfide, excess pressure, and an accidental release.

Table 3-26 presents examples of possible locations, conditions and process hazards which could potentially lead to a hydrogen sulfide release, and example controls for reducing the risk of such a release. The examples are intended to be illustrative, not exhaustive.

3.7.4 Storage and Handling

Hydrogen sulfide is classified as a flammable gas and poison. As such, it has several dangerous properties and should be handled and stored as any flammable gas. Because it is heavier than air, hydrogen sulfide will collect and concentrate in low-lying areas. It forms explosive mixtures with air over a wide range of conditions and also reacts explosively with some halogenated compounds. When heated to decomposition, it emits toxic fumes of oxides of sulfur.

TABLE 3-26. EXAMPLE CONDITIONS, PROCESS HAZARDS AND HAZARD CONTROLS IN HYDROGEN SULFIDE MANUFACTURING AND USE

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Vessels, pumps, piping	Corrosion including stress corrosion cracking, and hydrogen embrittlement	Equipment failure	Proper construction material selection Routine inspection and testing Verify the materials of construction for new equipment items by testing
Sulfide manufacturing reactor	Loss of cooling	Excessive exothermic reaction	Redundant temperature sensors with alarms Backup cooling system Adequate pressure relief Redundant flow control with automatic shutoff during upset
Combustion reactor or catalytic converter	Loss of temperature control	Overheating and overpressurization	Redundant temperature sensors with alarms Backup cooling system Adequate pressure relief Redundant flow control with automatic shutoff during upset

(Continued)

TABLE 3-26. (Continued)

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Process or storage vessels	Fire or explosion nearby	Loss of containment	Where possible, inert the vapor space on all process or storage vessels of flammable materials Hydrogen sulfide storage tanks isolated from potential sources of ignition Flammable gas detectors throughout process or storage areas Relief valves sized for heating due to fire
Reactor[1]	Loss of feed or composition control	Overpressurization leading to pressure relief discharge or equipment failure and release	Pressure relief; pressure alarm and interlocks with feed shutoff
Reactor[1]	Loss of temperature control	Excess temperature with overpressureization and same result as above	Pressure relief; redundant temperature measurement and alarms
Catalyst[2]	Deactivation of catalyst	Overpressurization with results as above	Pressure relief; monitoring feedstock specifications to prevent catalyst poisoning

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[1] Sodium Sulfide Production Process

[2] Mercaptan Production

Anhydrous (dry) hydrogen sulfide is noncorrosive to many commonly used materials of construction. However, moist or wet hydrogen sulfide is very corrosive to most metals. Table 3-27 lists construction materials suitable for hydrogen sulfide service. Hard steels, if highly stressed, are susceptible to hydrogen embrittlement by hydrogen sulfide. Additionally, hydrogen sulfide can produce severe sulfidation of metals at elevated temperatures and high strength steels may suffer stress corrosion cracking in the presence of moist hydrogen sulfide. Therefore, materials of construction must be carefully chosen to fit the service.

Steel or black iron pipe is commonly used for dry hydrogen sulfide (46). For wet hydrogen sulfide, aluminum and certain stainless steels are commonly used (46). Brass valves, although tarnished by hydrogen sulfide, hold up well in service. However, all lines carrying hydrogen sulfide are subject to corrosion and embrittlement and are prone to develop leaks.

Hydrogen sulfide may be shipped by rail, highway, water, or air. It can only be shipped in cylinders and TMU (ton multi-unit) tanks and tank cars that meet Department of Transportation (DOT) specifications (46). The cylinders must be retested hydrostatically every five years, and each tank must be equipped with a safety relief device of a fusible plug type that will yield at temperatures of 157-170 degrees Fahrenheit (46). The tanks must be leak-tight at 130 degrees Fahrenheit (46).

TABLE 3-27. MATERIALS OF CONSTRUCTION REPORTED TO BE ACCEPTABLE FOR HYDROGEN SULFIDE SERVICE

Material	For Wet or Dry H_2S	For Dry H_2S Only
Aluminum	X	
Brass		X
Carbon Steel		X
Copper		X
Copper-Nickel Alloys		X
Hastelloys®	X	
Inconel®		X
Lead		X
Nickel		X
Platinum	X	
Stainless Steel, Type 304		X
Stainless Steel, Type 310	X	
Stainless Steel, Type 316	X	
Tantalum	X	
Teflon®	X	
Titanium	X	

Source: Adapted from Reference 40

3.8 MECHLORETHAMINE

Mechlorethamine is reported to be a drug used in the treatment of cancer and also a former chemical warfare agent under the name of nitrogen mustard (24). It is a toxic liquid.

No information was found concerning the size of any U.S. market for medical applications of mechlorethamine. Mechlorethamine is reported to be produced at one site in the United States for use in military research (25).

3.8.1 Chemical Characteristics

Physical Properties and Hazards--

Mechlorethamine is a liquid at ambient conditions with a faint odor of herring. It is only slightly soluble in water. Table 3-28 lists a few of the physical properties of mechlorethamine that were found reported in the technical literature (24). As a liquid, the primary release hazard is liquid spills. Its low vapor pressure indicates that it probably poses little threat as an air toxic.

Chemical Properties and Reactivity and Hazards--

Little information has been reported concerning the chemical properties and reactivity of mechlorethamine; however, it is known that pure mechlorethamine decomposes on standing (24). Previous work has been unable to locate even such basic information as vapor pressure data, although with a reported boiling temperature of 189 °F at 18 mm Hg, the vapor pressure appears to be quite low and the normal boiling point is quite high. It would not appear, therefore, to pose a significant vapor threat if spilled at ambient conditions. Its very slight solubility in water, and its specific gravity slightly higher than water suggests that vapor emissions could be controlled by covering a spill with water. Of course, proper cleanup procedures would be required to prevent land or water runoff contamination. No specific information was found on whether or not this chemical is flammable.

TABLE 3-28. PHYSICAL PROPERTIES OF MECHLORETHAMINE

		Reference
CAS Registry Number	51-75-2	
Chemical Formula	$C_5H_{11}Cl_2N$	
Molecular Weight	156.07	24
Boiling Point	189°F @ 18 mm HG	24
Melting Point	-76°F	24
Specific Gravity (H_2O=1)	1.118 @ 77°F	24
Solubility in Water	Very slight	

Toxicological and Health Effects--

Mechlorethamine is reported to be a chemotherapy drug used in treating cancer (24). Toxic doses as low as 0.4 mg/kg have been reported in humans (20). The warning signs of mechlorethamine poisoning include: nausea, vomiting, bleeding, and skin lesions. Delayed effects can include hair loss, hearing loss, jaundice, impaired spermatogenesis and germinal aplasia, and hypersensitivity. Severe exposure can result in death.

3.8.2 Facility Descriptions

Mechlorethamine Manufacture--

No information on manufacture was found in the technical literature including a search through Chemical Abstracts. The general nature of this chemical suggests a batch chemical manufacturing procedure. As a result, no specific process features significantly heightening the generic release hazards of Section 2 can be identified.

Mechlorethamine Consumption--

Mechlorethamine is reported as currently used in research being conducted by the U.S. military and as a drug to treat cancer. (24)

3.8.3 Summary of Major Process Hazards and Control Technologies

There appears to be no specific information on the process characteristics of mechlorethamine manufacture or use in the open technical literature. Its toxicity suggests that all procedures are in accord with practices for other toxic substances which are covered in Section 2 of this manual and other technical literature. Fundamentally, selection of proper materials of construction, and special attention to the design, construction, operation, and maintenance details of equipment and procedures is required to minimize the chances for a release.

At ambient conditions, a release of mechlorethamine will result in a liquid spill. Proper containment by curbing or dikes around process equipment, and a method for absorbing or otherwise cleaning up a spill is required. Adequate ventilation should be provided to minimize inhalation of vapors. The toxicity of this chemical suggests that ultimate disposal of spill residues should avoid possible water or land contamination.

3.8.4 Storage and Handling

No information specific to the storage and handling of mechlorethamine was found in the technical literature surveyed. Since mechlorethamine is a liquid at room temperatures, storage and handling practices are expected to be those generic practices common to any toxic liquid. These practices have been discussed elsewhere in this manual. It has been reported that the undiluted liquid decomposes on standing.

3.9 METHIOCARB

Methiocarb is a broad spectrum carbamate pesticide. Little information is available concerning the size of the U.S. market for methiocarb. It is used solely as a pesticide in the United States and is manufactured at only one site in the United States.

3.9.1 Chemical Characteristics

Physical Properties--

Methiocarb is a white crystalline powder with a mild odor. It is soluble in acetone and alcohol, but is only slightly soluble in water. Table 3-29 lists a few of the physical properties of methiocarb.

Chemical Properties and Reactivity--

Little information is available concerning the chemical properties of methiocarb. However, it is known that methiocarb decomposes when heated, forming highly toxic nitrogen and sulfur oxides. In addition, methiocarb is unstable in highly alkaline media.

Toxicological and Health Effects--

Methiocarb is a highly toxic carbamate insecticide. The probable oral lethal dose for a human is approximately 50 to 500 ppm or between 1 teaspoon and 1 ounce for a 150-pound adult (24). Exposure can result in slowed heartbeat, blurred vision, slight paralysis, muscle twitching, nausea, vomiting, diarrhea, and abdominal pain. Acute exposure can result in unconsciousness, convulsions, and death.

3.9.2 Facility Descriptions

This subsection provides brief descriptions of the manufacture and uses of methiocarb in the United States.

TABLE 3-29. PHYSICAL PROPERTIES OF METHIOCARB

		Reference
CAS Registry Number	2-32-65-7	
Chemical Formula	$C_{11}H_{15}NO_2S$	
Molecular Weight	225.3	
Melting Point	243°F	24
Vapor Pressure	1×10^{-4} mm Hg	17
Solubility in Water	0.0027 lb/100 lb H_2O	17

Methiocarb Manufacture--

Little information is available concerning the manufacture of methiocarb; however, it is known that methiocarb can be manufactured by the reaction of methyl isocyanate and 4-methylthio-3,5-xylenol, although details of the process are confidential (45). A small-scale process has also been patented for laboratory synthesis (45).

Methiocarb Consumption--

Methiocarb is used as an insecticide, acaricide, and molluscicide. It is used for insect control on various types of fruits and vegetables and in bait pellets to control slugs and snails. It is also used as a bird repellent on corn seed, cherries, and blueberries.

3.9.3 Summary of Major Process Hazards and Control Technologies

The most important property of methiocarb that can promote equipment failure is its ability to decompose to nitrogen and toxic sulfur oxide gases on heating. Thus, loss of temperature control to any process vessel containing methiocarb could lead to overpressure and eventual equipment failure. The capacity and integrity of temperature control and cooling systems must therefore be carefully evaluated for systems that handle methiocarb. Redundant temperature sensors with alarms and backup cooling systems may be in order for some processes. Reaction feed flowrates should be limited so that a loss of mixing or cooling will not lead to thermal decomposition. This discussion is intended to be illustrative and not exhaustive. A discussion of hazard prevention and control appears in Section 2.

3.9.4 Storage and Handling

Little information is available concerning the storage and handling of methiocarb. It should be stored away from potential sources of fire since it decomposes on heating. It should be kept dry since the liquid solutions are also highly toxic.

3.10 METHYL BROMIDE

Methyl bromide is a colorless gas at typical room temperature and is a soil and space fumigant and as a chemical intermediate. Methyl bromide is produced by the esterification of methanol with hydrobromic acid. In 1983, it was estimated that 35 million pounds of methyl bromide were manufactured in the United States (18). At that time, the projected demand for 1987 was 25 million pounds (18). As of 1984, three manufacturers with capacities of 8, 30, and 35 million pounds of methyl bromide existed in the United States (18).

In 1984, the uses of methyl bromide manufactured in the United States were as follows: soil fumigant, 80 percent; space fumigant, 15 percent; and other uses, 5 percent.

3.10.1 Chemical Characteristics

Physical Properties and Hazards--

Methyl bromide is a colorless gas at ambient conditions, but it liquefies at moderate pressures. Table 3-30 lists the physical properties of methyl bromide.

Methyl bromide is only slightly soluble in water. The gas is 3.3 times more dense than air and will tend to stay close to the ground when released into the atmosphere. Because liquid methyl bromide has a large coefficient of thermal expansion, liquid-full equipment can pose the hazard of rupture on heating.

Chemical Properties and Hazards--

The most significant chemical properties of methyl bromide that can contribute to the potential for an accidental release are as follows:

- Flammability - Methyl bromide is flammable in air at concentrations from 10 to 16 percent methyl bromide.

TABLE 3-30. PHYSICAL PROPERTIES OF METHYL BROMIDE

		Reference
CAS Registry Number	74-83-9	
Chemical Formula	CH_3Br	
Molecular Weight	94.94	
Normal Boiling Point	38.41 °F @ 14.7 psia	33
Melting Point	-136.7 °F	33
Liquid Specific Gravity (H_2O=1)	1.732 @ 32 °F	50
Vapor Specific Gravity (air=1)	3.3 @ 68 °F	50
Vapor Pressure	27.5 psia @ 68 °F	50
Vapor Pressure Equation: $\log Pv = A - \frac{B}{T+C}$ where: Pv = vapor pressure, mm Hg T = temperature, °C A = 6.95965, a constant B = 986.590, a constant C = 238.32, a constant		51
Liquid Viscosity	0.324 Centipoise @ 77 °F	33
Solubility in Water	1.75 lb/100 lb solution @ 68 °F	50
Specific Heat at Constant Pressure	0.107 Btu/(lb-°F) @ 77 °F	33
Latent Heat of Vaporization	108.4 Btu/lb @ 38.4 °F	33
Average Coefficient of Thermal Expansion, 5-37°F	0.00163/°F	33
Liquid Surface Tension	25.5 dynes/cm @ 32 °F	51
Autoignition Temperature	998 °F	50
Explosive Range, Volume % in air	10 min. 16 max.	50

(Continued)

TABLE 3-30. (Continued)

		Reference
Properties useful in determining other properties from physical property correlations.		
Critical Temperature	318.2 °F	51
Critical Pressure	757 psia	51
Critical Density	38.09 lb/ft^3	51

- Decomposition - Thermal decomposition of methyl bromide to produce carbon monoxide, carbon dioxide, and highly toxic bromides can occur above 750 °F (39).

- Decomposition - In aqueous solution, methyl bromide can undergo hydrolysis to methanol and hydrobromic acid. The rate of hydrolysis increases in the presence of alkaline materials.

- Corrosivity - Most metals commonly used as materials of construction are inert to pure, dry methyl bromide. One exception is aluminum. However, in the presence of moisture or alcohols, corrosion of zinc, tin, and iron occurs.

Toxicological and Health Effects--

Methyl bromide is highly toxic by inhalation and skin absorption. It has very little odor or irritating effects, even at high concentrations, and thus gives no warning. It is a dangerous cumulative poison. Delayed symptoms that may appear several hours after inhalation include dizziness, headache, nausea, vomiting, abdominal pain, weakness, blurred vision, mental confusion, convulsions, collapse, and coma. Repeated exposure can cause central nervous system depression, kidney damage, and permanent brain damage. Severe exposure can result in fatal pulmonary edema. The International Agency for Research on Cancer (IARC) has determined that there is limited animal evidence and inadequate human evidence that methyl bromide is a carcinogen. The Occupational Safety and Health Administration (OSHA) standard in air for methyl bromide is a ceiling limit of 20 ppm. Workers should never be exposed to a concentration higher than this limit. The OSHA standard also notes that methyl bromide is harmful when absorbed through the skin (25). The LD_{50} for rats via ingestion is 214 mg/kg (25). Table 3-31 summarizes some of the relevant exposure data for methyl bromide.

TABLE 3-31. EXPOSURE LIMITS FOR METHYL BROMIDE

Limit	Concentration (ppm)	Description	Reference
IDLH	2,000	The concentration defined as posing an immediate danger to life and health (i.e., causes irreversible toxic effects for a 30-minute exposure).	23
PEL	20	A time-weighted 8-hour exposure to this concentration, as set by the Occupational Safety and Health Administration (OSHA), should result in no adverse effects for the average worker.	23
TC_{LO}	35	This concentration is the lowest published concentration causing toxic effects (irritation) for a 1-minute exposure.	20
LC_{LO}	60,000	This concentration is the lowest published lethal concentration for a human over a 2-hour exposure.	20

3.10.2 Facility Descriptions

This subsection provides brief descriptions of the manufacture and uses of methyl bromide in the United States. Section 3.7.3 discusses major accidental release hazards of these processes.

Methyl Bromide Manufacture--

Methyl bromide is manufactured primarily by the reaction of hydrobromic acid with methanol. Figure 3-15 is a flow diagram of a typical manufacturing process.

In this particular process, hydrobromic acid and methanol are fed to a reactor. The reaction is carried out in the presence of concentrated sulfuric acid (33). The crude reaction products are sent to a distillation column where methyl bromide is removed and methanol and hydrobromic acid are recycled to the reactor. The product is dried to remove residual water and is redistilled to remove impurities.

Processes also exist in which sulfuric acid is added to a solution of sodium bromide and methanol in a reactor to produce methyl bromide. The methyl bromide is then recovered in a manner similar to that discussed above.

Methyl Bromide Consumption--

Methyl bromide is used primarily as a soil fumigant, insecticide, rodenticide, and nematocide (18). In 1984, agricultural and related applications accounted for approximately 95% of the U.S. consumption. In addition to these agricultural uses, methyl bromide is used as an intermediate in the manufacture of pharmaceuticals and other agricultural chemicals, as a fire extinguishing agent, and also as a selective solvent.

3.10.3 Summary of Major Process Hazards and Control Technologies

To reduce the risk of an accidental release, specific measures broadly classified as prevention, protection or mitigation measures may be applied.

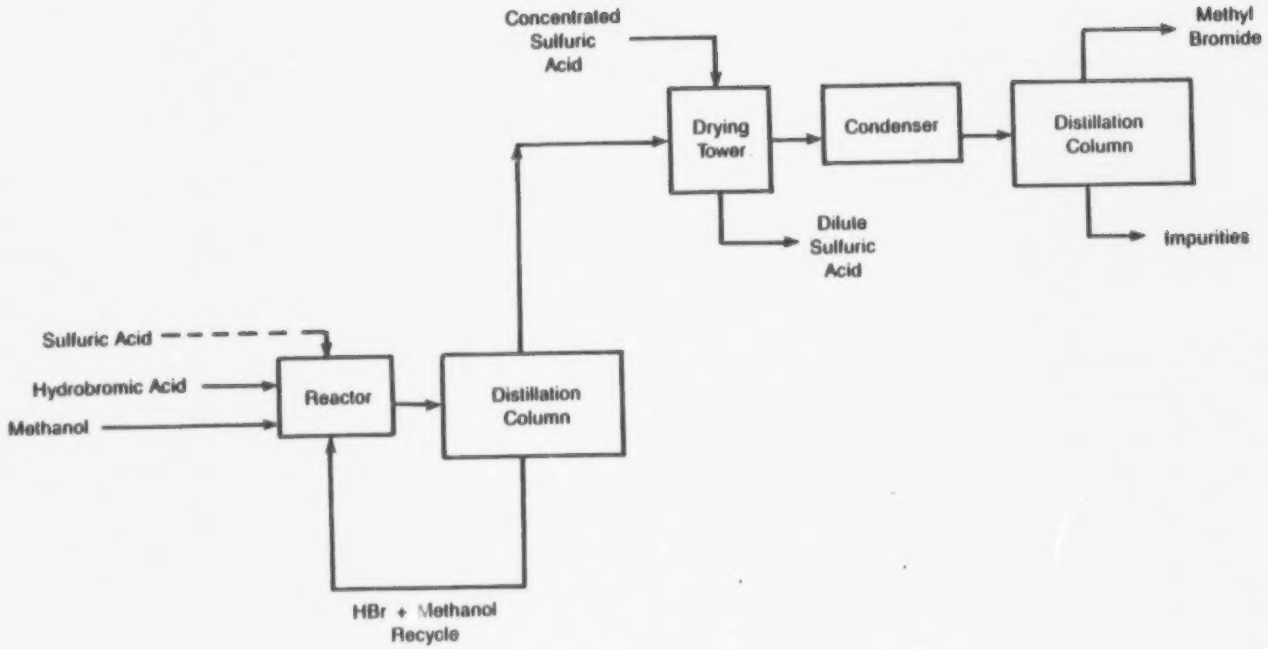

Figure 3-15. Conceptual flow diagram of typical methyl bromide manufacturing process.

Adapted from: Reference 33

These measures are discussed generally in Section 2 in this manual and are discussed in other technical literature. The properties of methyl bromide that contribute to the risk of a release are its relatively low boiling point, high vapor pressure, flammability and corrosivity.

The highest hazard area for this process appears to be the methyl bromide recovery column. An upset with this distillation column could lead to a methyl bromide release. Corrosion of process equipment could also result in an accidental release of methyl bromide from this process. The presence of sulfuric and hydrobromic acids in the process can be expected to cause corrosion problems. Inappropriate materials of construction could fail, resulting in an accidental release of methyl bromide.

Table 3-32 presents examples of locations, conditions and process hazards which could potentially lead to a methyl bromide release, as well as example controls for reducing the risk of such a release. The examples are intended to be illustrative, not exhaustive.

3.10.4 Storage and Handling

Methyl bromide is stored as a liquefied gas in pressure vessels because of its relatively low boiling point and high vapor pressure. Methyl bromide is also stored in cylinders for small-scale use and is shipped by tank car. Since no pressure relief devices are used on cylinders containing methyl bromide (53), all sources of heat must be kept away from cylinders to prevent hydrostatic pressure buildup from leading to overpressure (52).

Table 3-33 lists materials of construction reported to be suitable for methyl bromide service. It is not particularly corrosive to most metals and is noncorrosive when completely dry. However, when aluminum and aluminum alloys are attacked by methyl bromide, aluminum trimethyl is formed, which is spontaneously combustible.

TABLE 3-32. EXAMPLE CONDITIONS, PROCESS HAZARDS, AND HAZARD CONTROLS IN METHYL BROMIDE MANUFACTURING AND USE

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Methyl bromide product distillation units	Loss of condenser cooling	Overpressurization	Reboiler heating interlocked to temperature sensors on condenser Adequately-sized pressure relief Relief discharge to a flare or scrubber
	Excess methyl bromide feed	Overfilling; overpressurization	High level sensor and alarm interlocked with feed flow controller Feed flow restrictors Overflow catch tank Improved operator training and operating procedures
Process or storage	Fire or explosion nearby	Overheating and overpressurization	Flammable gas detectors around process and storage areas Adequate fire protection Relief valve sized for heating due to fire Tanks, vessles, and storage cylinders isolated from flammable materials and sources of ignition

(Continued)

TABLE 3-32. (Continued)

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Storage vessel lines	Backflow of water to storage vessels	Corrosion and equipment failure	Rarely used or unnecessary water lines disconnected or blinded off Check valves or feed tanks in essential water lines Routine corrosion inspection
	Inadequate water removal from methyl bromide product	Corrosion and equipment failure	Routine corrosion inspection Improved materials of construction for high risk equipment.

TABLE 3-33. MATERIALS OF CONSTRUCTION REPORTED TO BE SUITABLE FOR METHYL BROMIDE SERVICE

Brass
Copper
Hastelloy-B®
Hastelloy-C®
Inconel®
Lead
Mild Steel
Monel®
Nickel
Silver
Stainless Steel
Titanium
Zirconium

Source: Adapted from Reference 26

3.11 SODIUM AZIDE

Sodium azide is a chemical intermediate used in the manufacture of pharmaceuticals. It is also used as an explosive, herbicide, fungicide, nematicide, and soil fumigant.

No information was found concerning the size of the U.S. market for sodium azide; however, it is reported as not currently being manufactured at any site in the United States (53).

3.11.1 Chemical Characteristics

Physical Properties and Hazards--

Sodium azide is a colorless solid. It is soluble in water, slightly soluble in ethyl alcohol and benzene, and insoluble in ether. Table 3-34 lists the physical properties of sodium azide. As a solid, dust or fumes from process operations present the major air release hazard.

Chemical Properties and Hazards--

Sodium azide is a combustible solid (54). It can decompose explosively on heating, shock, concussion, or friction (54). Decomposition products consist of nitrogen oxides, which are extremely explosive. Sodium azide reacts with copper, silver, mercury, and lead to form explosive azides. It can form highly toxic hydrazoic acid fumes in the event of a fire. In addition, sodium azide is incompatible with bromine, benzoyl chloride, potassium hydroxide, carbon disulfide, sulfuric acid, and nitric acid (54). Its overall reactivity and chemical instability contribute significantly to an accidental release hazard, since these attributes could set off a chain of events leading to a release.

Toxicological and Health Effects--

Sodium azide is highly toxic by ingestion, inhalation and skin absorption. Ingestion or inhalation can result in dizziness, weakness, blurred vision, shortness of breath, hypertension, slowed heart rate, abdominal pain

TABLE 3-34. PHYSICAL PROPERTIES OF SODIUM AZIDE

		Reference
CAS Registry Number	26628-22-8	
Chemical Formula	NaN_3	
Molecular Weight	65.02	
Melting Point	Decomposes at 572 °F	54
Specific Gravity (H_2O=1)	1.85 @ 68 °F	24
Solubility in Water	42 lb/100 lb H_2O @ 63 °F	24

and reduced body temperature and pH. Acute exposure can result in convulsion, unconsciousness, and death. Skin contact can result in redness and pain. When sodium azide is absorbed through the skin, it produces symptoms similar to those of inhalation or ingestion. The only exposure limit established for sodium azide to date has been a Threshold Limit Value (TLV) of 0.1 ppm, as set by the American Conference of Governmental Industrial Hygienists (ACGIH) (24). The LD_{50} for rats via oral routes is 27 mg/kg (25).

3.11.2 Facility Descriptions

This subsection provides brief descriptions of the manufacture and uses of sodium azide in the United States. Major accidental release hazards of these processes are discussed in Section 3.11.3.

Sodium Azide Manufacture--

Sodium azide has been manufactured by a liquid ammonia process in the United States. Figure 3-16 is a flow diagram of a typical manufacturing process.

In this process, sodium reacts with liquid ammonia in the presence of a catalyst such as ferric nitrate, to form sodamide. The sodamide, along with nitrous oxide, is fed to a reactor where sodium azide, sodium hydroxide, and additional ammonia are produced. The reaction is typically carried out at a temperature of approximately 86 °F (55). The ammonia produced during the reaction is vented from the reactor. The sodium azide product is then separated from the caustic solution by crystallization from water.

Sodium Azide Consumption--

Sodium azide is used primarily as an intermediate chemical in the manufacture of pharmaceuticals. It is also used as an explosive, and has been used as a herbicide, fungicide, nematicide, and soil fumigant. Other end uses of sodium azide include: propellant for inflating automotive air bags, retarder in the manufacture of sponge rubber, anticoagulant in styrene and butadiene latexes, a reagent in water pollution analysis, and an intermediate

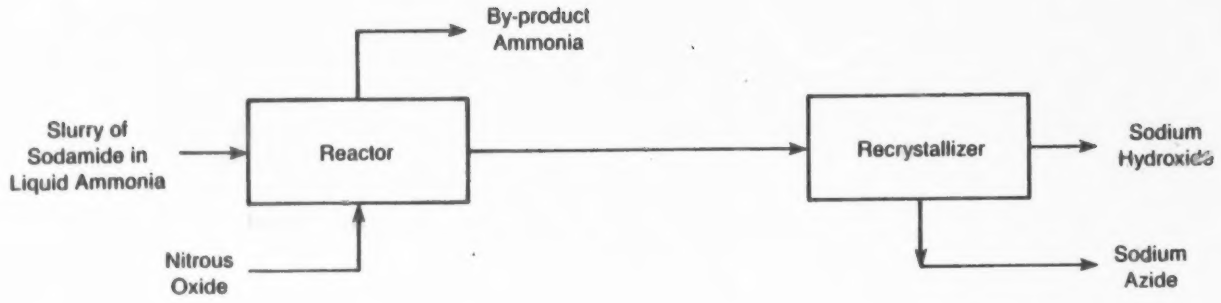

Figure 3-16. Conceptual flow diagram of typical sodium azide manufacturing process.

Adapted from: Reference 33

in organic synthesis. Limited information is available on the various uses of sodium azide since most are small, limited-scale uses.

3.11.3 Summary of Major Process Hazards and Control Technologies

To reduce the risk of an accidental release, specific measures broadly classified as prevention, protection or mitigation measures may be applied. These measures are discussed generally in Section 2 in this manual and are described in other technical literature.

The most important property of sodium azide that can promote equipment failure is its ability to decompose explosively on heating, shock, concussion, or friction. Thus, loss of temperature control to any process vessel containing sodium azide could result in explosion and equipment failure. Redundant temperature sensor and controllers should be used in high-temperature applications.

The product recrystallizer is the manufacturing process location with the greatest potential for an accidental release. Spills or leaks of material from the crystallizer would result in a solids contamination of the air by dust or fumes, and of the surrounding area by solids deposition.

The primary release hazard in its use as an intermediate chemical is careless storage and handling of the solid chemical.

Sodium azide must be stored away from heat sources since it is a combustible solid and can explode on heating, shock, concussion, or friction. Care must therefore be taken when sodium azide is transferred from a storage container to a process. Large inventories of sodium azide should be located away from other process areas. Blast shielding may be considered where sodium azide must be routinely handled.

A special hazard with sodium azide is the possible accumulation of the solid in inadequately cleaned equipment and facility areas. Proper employee training and well-documented procedures are essential when handling sodium azide. Inadequate fire protection in process or storage areas could also lead to loss of containment. Process or storage areas should be protected with sprinkler systems, and blast shields may be appropriate for some applications.

Table 3-35 presents examples of possible locations, conditions and process hazards which could potentially lead to a sodium azide release, as well as example controls for reducing the risk of such a release. This discussion is intended to be illustrative, not exhaustive.

3.11.4 Storage and Handling

Limited information is available concerning the storage and handling of sodium azide. It is stored in polyethylene or similar type drums (54), and it is compatible with most common materials of construction, but as noted in Section 3.11.1, it reacts with a number of metals to form extremely explosive azides.

TABLE 3-35. EXAMPLE CONDITIONS, PROCESS HAZARDS AND EXAMPLE HAZARD CONTROLS IN SODIUM AZIDE MANUFACTURING AND USE

Location	Condition	Process Hazard Leading or Release	Examples of Hazard Controls
Sodium Azide Product Recrystallizer	Solids contamination by dust or fumes	Accummulation of solids on equipment can lead to conditions where heating, shock, concussion, or friction could lead to explosive decomposition; the resulting damage can lead to an accidental release	Good housekeeping; employee training; locate large inventories away from other process areas; blast shielding for routine handling areas; sprinkler systems
Storage and Handling Areas	Solids contamination by dust	(see above)	(see above)
	Fire	Heating of stored solids leading to explosion and release of toxic solids	Adequate fire protection
Process Vessel	Loss of temperature control	Explosion and equipment failure	Redundant temperature sensor and controllers in high-temperature applications

3.12 TETRAETHYL TIN

Tetraethyl tin is reported to be used as a pesticide, and may have applications as a catalyst, and preservative for wood, textiles, paper and leather (24). It is reported as not being a registered pesticide in the U.S. (24). Little information is available concerning the size of the U.S. market for tetraethyl tin; it is not currently being manufactured in the United States, although it can be manufactured on request at one site. It has also been reported as having no commercial utility (33).

3.12.1 Chemical Characteristics

Physical Properties and Hazards--

Tetraethyl tin is a colorless liquid at ambient conditions. It is very slightly soluble in water and is soluble in most organic solvents. Table 3-36 lists the physical properties of tetraethyl tin. Its boiling point is high, so it does not represent a substantial air release hazard at typical ambient conditions.

Chemical Properties and Hazards--

Little information is available concerning the chemical properties and reactivity of tetraethyl tin; however, it is known that tetraethyl tin decomposes on heating, emitting acrid smoke and fumes (24). It is incompatible with strong oxidizers.

Toxicological and Health Effects--

Tetraethyl tin is highly toxic by inhalation and ingestion. The warning signs of exposure include: muscular weakness and paralysis leading to respiratory failure, convulsions, headaches, dizziness, physiological and neurological disturbances, sore throat, cough, abdominal pain, nausea, and vomiting. Acute exposure can cause swelling of the brain and spinal cord and eventual death. The Occupational Health and Safety Administration (OSHA) has set a short term exposure limit (STEL) of 0.1 mg (tin)/ m^3 (25). The LD50 for rats via ingestion is 16 mg/kg (25).

TABLE 3-36. PHYSICAL PROPERTIES OF TETRAETHYL TIN

		Reference
CAS Registry Number	597-64-8	
Chemical Formula	$C_8H_{20}Sn$	
Molecular Weight	234.97	
Boiling Point	357.8 °F @ 14.7 psia	24
Melting Point	-169.6 °F	24
Specific Gravity (H_2O=1)	1.199 @ 68 °F	24

3.12.2 Facility Descriptions

This subsection briefly describes the manufacture and uses of tetraethyl tin in the United States. Major accidental release hazards of these processes are discussed in Section 3.12.3.

Tetraethyl Tin Manufacture--

Limited information is available concerning the manufacture of tetraethyl tin. Although it is not presently produced in the United States, several processes have been patented for its manufacture (56,57).

In a typical process, finely divided tin and sodium tetraethylaluminum dissolved in toluene are fed to a reactor equipped with an external heating source (e.g., steam jacket), agitator, and a nitrogen pad system. The reaction mixture is heated to approximately 120 to 140°F and ethyl chloride is added (20). The reaction is carried out for a period of 1.5 hours. The reaction mixture is then cooled to room temperature, filtered to remove sodium chloride by-product, and vacuum distilled to remove the toluene and triethylaluminum overhead. The residual liquid is the desired tetraethyl tin product.

Tetraethyl Tin Consumption--

Tetraethyl tin has no significant commercial uses (33). It has been used as a biocide, bactericide, fungicide, insecticide, catalyst, and preservative for wood, textile, paper, and leather in the past. It has also been used to induce encephalopathy (a disease of the brain) and intracranial pressure in laboratory animals for research purposes (33).

3.12.3 Summary of Major Process Hazards and Control Technologies

The most important property of tetraethyl tin that can promote equipment failure is its ability to decompose to acrid vapor on heating. Thus, loss of temperature control in any process vessel containing tetraethyl tin could lead to overpressure and eventual equipment failure. Redundant temperature sensors and controllers should be used in any high-temperature processes where teraethyl tin is used. A general discussion of hazard prevention and control appears in Section 2 in this manual and are discussed in greater detail in other technical literature.

3.12.4 Storage and Handling

No information is currently available on the storage and handling of tetraethyl tin. As a hazardous liquid, standard storage practices for such materials should be followed.

3.13 TRICHLOROACETYL CHLORIDE

Trichloroacetyl chloride is an intermediate chemical used to manufacture other chemicals. The chemical characteristics, storage, uses, and manufacture of trichloroacetyl chloride are discussed in this section of the manual, as well as the major hazards of these processes.

No information is currently available on the size of the U.S. market for trichloroacetyl chloride.

3.13.1 Chemical Characteristics

This subsection describes the physical, chemical, and toxicological properties of trichloroacetyl chloride as they relate to accidental releases.

Physical Properties and Hazards--

Trichloroacetyl chloride is a colorless liquid at ambient conditions. Table 3-37 lists the physical properties of trichloroacetyl chloride.

Chemical Properties and Hazards--

Two chemical properties of trichloroacetyl chloride contribute to the potential for an accidental release of the chemical:

- Decomposition - Trichloroacetyl chloride decomposes on contact with water to form highly corrosive chloroacetic and chlorohydric acids (52). This hydrolysis reaction can occur violently.

- Flammability - Trichloroacetyl chloride may burn but does not ignite readily (24).

Toxicological and Health Effects--

Little information is available concerning the toxic effects of accidental exposure to trichloroacetyl chloride; however, trichloroacetyl chloride is

TABLE 3-37. PHYSICAL PROPERTIES OF TRICHLOROACETYL CHLORIDE

		Reference
CAS Registry Number	76-02-8	
Chemical Formula	CCl_3COCl	
Molecular Weight	181.83	
Boiling Point	244°F @ 14.7 psia	21
Melting Point	-70 °F	52
Liquid Specific Gravity (H_2O=1)	1.6202 @ 68 °F	58
Vapor Pressure	0.306 psia @ 68 °F	21

Vapor Pressure Equation:

$$\log Pv = A - \frac{B}{T+C}$$

where: Pv = vapor pressure, mm Hg
T = temperature, °C
A = 6.99075, a constant
B = 1,390.47, a constant
C = 220.11, a constant

Solubility in Water	Decomposes	21

toxic by ingestion and inhalation. It is also a strong irritant to the skin and may cause severe burns. The LD_{50} for rats via ingestion is 600 mg/kg (25).

3.13.2 Facility Descriptions

This subsection briefly describes the manufacture and uses of trichloroacetyl chloride in the United States. Major accidental release hazards of these processes are discussed in Section 3.13.4.

Trichloroacetyl Chloride Manufacture--

Trichloroacetyl chloride is manufactured by the reaction of a polyhalomethane with carbon monoxide in the presence of a platinum or palladium triad catalyst.

In a typical process, a mixture of palladium chloride catalyst and carbon tetrachloride is fed to a reactor. Carbon monoxide is then fed to the reactor. The reactor is operated at a temperature in the range of 300-400 °F and at a pressure of approximately 100 atmospheres (59). On completion of the reaction, the reactor is vented and the reaction products are filtered to remove any residual solid catalyst. The filtrate is then distilled to remove any unreacted carbon tetrachloride, leaving the desired trichloroacetyl chloride product. The unreacted carbon tetrachloride is subsequently returned to the reactor.

Trichloroacetyl Chloride Consumption--

Little information is available on the use of trichloroacetyl chloride; however, it used as an intermediate in the manufacture of other chemicals.

3.13.3 Summary of Major Process Hazards and Control Technologies

To reduce the risk of an accidental release of specific measures broadly classified as prevention, protection or mitigation measures may be applied.

Section 2 discusses the general features of these measures and details are presented elsewhere in the technical literature.

The properties of trichloroacetyl chloride that contribute to the risk of a release are its corrosiveness and its reactivity with water. The primary hazard areas in the manufacturing process appear to be the reactor and distillation column where trichloroacetyl chloride is present at an elevated temperature. The reactor is likely to be more hazardous than the distillation column because it operates at very high pressure. Any failure in this system could release large quantities of hot trichloroacetyl chloride vapor.

Table 3-38 presents examples of possible locations, conditions and process hazards which could potentially lead to a trichloroacetyl chloride release and example controls for reducing the risk of such a release. The examples are intended to be illustrative, not exhaustive.

3.13.4 Storage and Handling

Dry trichloroacetyl chloride is relatively noncorrosive to most metals. However, in the presence of moisture, trichloroacetyl chloride is highly corrosive and is similar to chloroacetic acid in its corrosive effects. Thus, storage vessels and containers must be constructed of materials that take this potential corrosion effect into account. Trichloroacetyl chloride is typically shipped and stored in metallic drums lined with a polyethylene or similar coating.

TABLE 3-38. EXAMPLE CONDITIONS, PROCESS HAZARDS AND HAZARD CONTROLS IN TRICHLOROACETYL CHLORIDE MANUFACTURING AND USE

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Trichloroacetyl chloride reactor	Loss of temperature control	Equipment failure	Temperature and pressure sensors with alarms Routine inspection and testing of high pressure equipment. Pressure relief system
Process or storage vessels	Inadequate water removal from feeds to vessels	Corrosion, exothermic reactions and equipment failure	Routine inspection and testing of all equipment handling chloroacetyl chloride Periodic or continuous monitoring for water contamination
Process or storage vessels	Backflow of water into vessels	Exothermic reaction and overpressurization	Blind or disconnect rarely used or unnecessary water lines Redundant check valves in essential water lines Pressure relief on high risk piping Relief sent to vent to a scrubber or collection tank

(Continued)

TABLE 3-38. (Continued)

Location	Condition	Process Hazard Leading to Release	Examples of Hazard Controls
Any process vessel containing chloroacetyl chloride	Mixing of water with chloroacetyl chloride, due to leaking process vessel jacket or steam-filled heat exchanger tube	Corrosion leading to equipment failure and release	Non aqueous heating or cooling fluid Routinely inspect and test all jacketed equipment Pressure relief on jackets and heat exchangers that vent to a collection tank or scrubber

SECTION 4
REFERENCES

1. Battelle Columbus Division. Guidelines for Hazard Evaluation Procedures. The Center for Chemical Process Safety, American Institute of Chemical Engineers, New York, NY, 1985.

2. Lees, Frank P. Loss Prevention in the Process Industries, Volumes 1 and 2, Butterworths, London, England, 1983.

3. Process Safety Management, Control of Acute Hazards. Chemical Manufacturer's Association, Washington, DC, May 1985.

4. Green, D.W. (ed.). Perry's Chemical Engineer's Handbook. Chemical Manufacturers Association, Washington, DC, May 1985.

5. Federal Register. Volume 50. April 16, 1985. pp. 14,941-14,945.

6. Bennett, G.F., F.S. Feates, and I. Wilder. Hazardous Materials Spills Handbook. McGraw-Hill Book Company, New York, NY, 1982.

7. Eggleston, L.A., W.R. Herrera, and M.D. Pish. Water Spray to Reduce Vapor Cloud Spray. Loss Prevention, Volume 10, American Institute of Chemical Engineers, New York, NY, 1976.

8. Watts, J.W. Effects of Water Spray on Unconfined Flammable Gas. Loss Prevention, Volume 10, American Institute of Chemical Engineers, New York, NY, 1976.

9. Vincent, G.C., et al. Hydrocarbon Mist Explosions - Part II, Prevention by Water Fog. Loss Prevention, Volume 10, American Institute of Chemical Engineers, New York, NY, 1976.

10. Experiments With Chlorine. Ministry of Social Affairs, Voorburg, Netherlands, 1975.

11. Martinsen, W.E. and S.P. Muhlenkamp. Disperse LNG Vapors With Water. Hydrocarbon Processing, July 1977.

12. Moore, P.A.C. and W.D. Rees. Forced Dispersion of Gases by Water and Steam. Inst. Chem. Engineers Symposium Proceedings. The Containment and Dispersion of Gases by Water Sprays. Manchester, England, 1981.

13. Moodie, K. The Use of Water Spray Barriers to Disperse Spills of Heavy Gases. Plant/Operations Progress, October 1985.

14. Moodie, K. Experimental Assessment of Full-Scale Water Spray Bariers for Dispersing Dense Gases. Inst. Chem. Engineers Symposium Proceedings. The Containment and Dispersion of Gases by Water Sprays. Manchester, England, 1981.

15. Stus, T.F. On Writing Operating Instructions. Chemical Engineering, November 26, 1984.

16. Burk, A.F. Operating Procedures and Review. Presented at the Chemical Manufacturers Association Process Safety Management Workshop. Arlington, VA, May 7-8, 1985.

17. World Chemical Outlook. Chemical and Engineering News, December 15, 1986.

18. Chemical Products Synopsis. Manneville Chemical Products Corporation, Cortland, NY, 1985.

19. McKetta, J. Encyclopedia of Chemical Processing and Design. Marcel Dekker Publishing Company, New York, NY, 1985.

20. Lewis, R.J.S. and R.L. Tatken (ed.). Registry of Toxic Effects of Chemical Substances. NIOSH (DHEW) Publication No. 79-100, January 1985.

21. Dean, J. (ed.). Lange's Handbook of Chemistry. Twelfth Edition, McGraw-Hill Book Company, New York, NY, 1979.

22. Acrylontrile Data Sheet. E.I. Dupont de Nemours & Company (Inc.), Wilmington, DE, 1987.

23. NIOSH/OSHA Pocket Guide to Chemical Hazards. DHEW (NIOSH) Publication No. 78-210.

24. Chemical Emergency Preparedness Program Interim Guidance. Chemical Profiles, 2 Volumes. U.S. Environmental Protection Agency, Washington, DC, December 1985.

25. Lewis, R.J. and R.L. Tatken, (ed.). Registry of Toxic Effects of Chemical Substances. Microfiche Ed. National Institute for Occupational Safety and Health. Cincinnati, OH. April 1987.

26. Schweitzer, P.A. Corrosion Resistance Tables. Marcel Dekker, Inc., New York, NY, 1976.

27. Hazardous Substances Databank. National Library of Medicine, Bethesda, MD, July 1985.

28. Material Safety Data Sheet. Moby Corporation, Pittsburgh, PA, March 1986.

29. Vapor Pressure Data Provided by Occidental Chemical Corporation, Niagara Falls, NY, November 1983.

30. Benzotrichloride Data Sheet 728G 1284. Occidental Chemical Corporation, Niagara Falls, NY, November 1983.

31. Sax, N.I. Dangerous Properties of Industrial Materials. Sixth Edition. Van Nostrand Rienhold Company, New York, NY, 1984.

32. Material Safety Data Sheet. Occidental Chemical Corporation, Niagara Falls, NY, October 1985.

33. Kirk, R.E. and Othmer, D.F. Encyclopedia of Chemical Technology. Third Edition, John Wiley & Sons, Inc., New York, NY, 1980.

34. U.S. Patent 3,974,093.

35. Shearson, W.H., H.E. Hall, and J.E. Stevens, Fine Chemicals from Coal. Ind. Eng. Chem. 41 (9), 1812-20 (1949).

36. Lawler, G.M. (ed.) Chemical Orgins and Markets. Fifth Edition. Chemical Information Services, Stanford Research Institute, 1977.

37. Chemical Profile, Chloracetic Acid. Chemical Marketing Reporter. Schnell Publishing Company, Inc., June 16, 1986.

38. U.S. Department of Health and Human Services. NIOSH Pocket Guide to Chemical Hazards. National Institute for Occupational Safety and Health. September 1985.

39. Gerhartz, W. (ed.). Ullmann's Encyclopedia of Industrial Chemistry. Fifth Edition, VCH Publishers, New York, NY, 1986.

40. Hamner, N.E. Corrosion Data Survey. Fifth Edition, National Association of Corrosion Engineers, 1974.

41. Terrill, James B., Ph.D., D.A.B.T. Acute Inhalation Toxicity Study with Furan in the Rat. Final Report. Hazelton Laboratories America, Inc., April 24, 1987.

42. Williams, A. Furans - Synthesis and Applications. Noyes Data Corporation, London, England, 1973.

43. Handling Hazardous Materials. Report No. NASA SP-5032. National Aeronautics and Space Administration, Greenbelt, MD, 1965.

44. The Handling and Storage of Liquid Propellants. Office of the Director of Defense Research and Engineering. U.S. Advisory Panel on Fuels and Lubricants, Washington, DC, 1961.

45. Sittig, M. Pesticide Manufacturing and Toxic Materials Control Encyclopedia. Noyes Data Corporation, NJ, 1980.

46. Handbook of Compressed Gases. Second Edition, Compressed Gas Association, Inc., New York, NY, 1981.

47. Lawler, G.M. (ed.). Chemical Orgins and Markets. Fifth Edition Chemical Information Services, Stanford Research Institute, 1977.

48. Paskall, Harold G. Capability of the Modified Claus Process. Prepared for Alberta Department of Energy and Natural Resources. Prepared by Western Research, Calgary, Alberta, March 1979.

49. Trofe, T.W., Dalrymple, D.A., and Scheffel, F.A. Stretford Status and R&D Needs. Gas Research Institute, Chicago, IL, February 1987.

50. Material Safety Data Sheet. Union Carbide Corporation, Danbury, CT, 1985.

51. Matheson Gas Book. Matheson Gas Products, Inc. Secaucus, NJ.

52. Material Safety Data Sheet. Rhone-Poulenc, Inc., Monmouth Junction, NJ, 1987.

53. 1986 Directory of Chemical Producers. Stanford Research Institute International, Menlo Park, CA.

54. Material Safety Data Sheet. Mallinckrodt, Inc., Paris, KY, 1985.

55. Filbert, W.F. and Acken, M.F. U.S. Patent No. 2,373,800.

56. U.S. Patent No. 3,057,894.

57. U.S. Patent No. 3,028,320.

58. Weast, R.C. (ed.). CRC Handbook of Chemistry and Physics. CRC Press, Inc., Boca Raton, FL, 1983.

59. U.S. Patent No. 3,454,632.

APPENDIX A

GLOSSARY

This glossary defines selected terms used in the text of this manual which might be unfamiliar to some users or which might be used differently by different authors.

Accidental Release: The unintentional spilling, leaking, pumping, purging, emitting, emptying, discharging, escaping, dumping, or disposing of a toxic material into the environment in a manner that is not in compliance with a plant's federal, state, or local environmental permits and results in toxic concentrations in the air that are a potential health threat to the surrounding community.

Assessment: The process whereby the hazards which have been identified are evaluated in order to provide an estimate of the level of risk.

Autocatalytic: A chemical reaction which is catalyzed by one of the products of the reaction.

Carcinogen: A cancer causing substance.

Containment/Control: A system to which toxic emissions from safety relief discharges are routed to be controlled. A caustic scrubber and/or flare can be containment/control devices. These systems may serve the dual function of destructing continuous process exhaust gas emissions.

Control System: A system designed to automatically maintain all controlled process variables within a prescribed range.

Emergency Response Plan: A plan of action to be followed by source operators after a toxic substance has been accidentally released to the atmosphere. The plan includes notification of authorities and impacted population zones, minimizing the quantity of the discharge, etc.

Exothermic: A term used to characterize the evolution of heat. Specifically refers to chemical reactions from which heat is evolved.

Facility: A location at which a process or set of processes are used to produce, refine or repackage chemicals, or a location where a large enough inventory of chemicals are stored so that a significant accidental release of a toxic chemical is possible.

Fire Monitor: A mechanical device holding a rotating nozzle, which emits a stream of water for use in firefighting. Fire monitors may be fixed in place or may be portable. A fire monitor allows one person to direct water on a fire whereas a hose of the same flowrate would require more than one person.

Hazard: A source of danger. The potential for death, injury or other forms of damage to life and property.

Hygroscopic: Readily taking up and retaining moisture (water).

Identification: The recognition of a situation, its causes and consequences relating to a defined potential, e.g., Hazard Identification.

Lachrymator: A substance which increases the flow of tears.

Mitigation: Any measure taken to reduce the severity of the adverse effects associated with the accidental release of a hazardous chemical.

Mutagen: An agent that causes biological mutation.

Plant: A location at which a process or set of processes are used to produce, refine, or repackage chemicals.

Prevention: Design and operating measures applied to a process to ensure that primary containment of toxic chemicals is maintained. Primary containment means confinement of toxic chemicals within the equipment intended for normal operating conditions.

Primary Containment: The containment provided by the piping, vessels and machinery used in a facility for handling chemicals under normal operating conditions.

Probability/Potential: A measure, either qualitative or quantitative, that an event will occur within some unit of time.

Process: The sequence of physical and chemical operations for the production, refining, repackaging or storage of chemicals.

Process Machinery: Process equipment, such as pumps, compressors, heaters, or agitators, that would not be categorized as piping and vessels.

Protection: Measures taken to capture or destroy a toxic chemical that has breached primary containment, but before an uncontrolled release to the environment has occurred.

Pyrophoric: A substance that spontaneously ignites in air at or below room temperature without supply of heat, friction, or shock.

Qualitative Evaluation: Assessing the risk of an accidental release at a facility in relative terms; the end result of the assessment being a verbal description of the risk.

Quantitative Evaluation: Assessing the risk of an accidental release at a facility in numerical terms; the end result of the assessment being some type of number that reflects risk, such as faults per year or mean time between failures.

Reactivity: The ability of one chemical to undergo a chemical reaction with another chemical. Reactivity of one chemical is always measured in reference to the potential for reaction with itself or with another chemical. A chemical is sometimes said to be "reactive", or have high "reactivity", without reference to another chemical. Usually this means that the chemical has the ability to react with common materials such as water, or common materials of construction such as carbon steel.

Redundancy: For control systems, redundancy is the presence of a second piece of control equipment where only one would be required. The second piece of equipment is installed to act as a backup in the event that the primary piece of equipment fails. Redundant equipment can be installed to back up all or selected portions of a control system.

Risk: The probability that a hazard may be realized at any specified level in a given span of time.

Secondary Containment: Process equipment specifically designed to contain material that has breached primary containment before the material is released to the environment and becomes an accidental release. A vent duct and scrubber that are attached to the outlet of a pressure relief device are examples of secondary containment.

Teratogenic: Causing anomalies of formation or development.

Toxicity: A measure of the adverse health effects of exposure to a chemical.

APPENDIX B

TABLE B-1. METRIC (SI) CONVERSION FACTORS

Quantity	To Convert From	To	Multiply By
Length:	in.	cm	2.54
	ft	m	0.3048
Area:	in.^{2}	cm^2	6.4516
	ft^2	m^2	0.0929
Volume:	in.^{3}	cm^3	16.39
	ft^3	m^3	0.0283
	gal.	m^3	0.0038
Mass (weight):	lb	kg	0.4536
	short ton (ton)	Mg	0.9072
	short ton (ton)	metric ton (t)	0.9072
Pressure:	atm	kPa	101.3
	mm Hg	kPa	0.133
	psia	kPa	6.895
	psig	kPa*	(psig)+14.696) x(6.895)
Temperature:	°F	°C*	(5/9)x(°F-32)
	°C	K*	°C+273.15
Caloric Value:	Btu/lb	kj/kg	2.326
Enthalpy:	Btu/lbmol	kj/kgmol	2.326
	kcal/gmol	kj/kgmol	4.184
Specific-Heat Capacity:	Btu/lb-°F	kj/kg-°C	4.1868
Density:	lb/ft^3	kg/m^3	16.02
	lb/gal.	kg/m^3	119.8
Concentration:	oz/gal.	kg/m^3	
	qt/gal.	cm^3/m^3	25,000
Flowrate:	gal./min	m^3/min	0.0038
	gal./day	m^3/day	0.0038
	ft^3/min	m^3/min	0.0283
Velocity:	ft/min	m/min	0.3048
	ft/sec	m/sec	0.3048
Viscosity:	centipose (CP)	kg/m-s	0.001

*Calculate as indicated.